

AD 728039

# **DEVELOPMENT OF FASTENER COUNTERSINK CORROSION PROTECTION SEALS**

**FINAL REPORT**

**(24 January 1970 to 24 April 1971)**

**APRIL 1971**

By

**G. W. Kelly**

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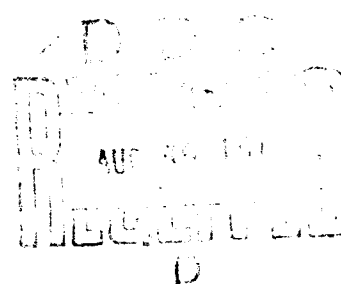
**NAVAL AIR SYSTEMS COMMAND  
DEPARTMENT OF THE NAVY**

By

**VOUGHT AERONAUTICS  
LTV AEROSPACE CORPORATION**

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<p>The objects of this program were to modify coating materials for use with specialized application equipment, to study application techniques applicable to production practices and to develop a color stable (non-yellowing) material suitable for this use. All objectives were oriented toward development of an elastomeric sealant system designed for use in sealing fastener-head countersinks in highly loaded aircraft skins that are susceptible to exfoliation corrosion.</p> <p>Materials were formulated that could be smoothly deposited on vertical surfaces to thicknesses of 5 to 7 mils per pass utilizing vapor-carrier type spray equipment; other materials formulated for use in conventional application equipment were easily applied to an aesthetically smooth finish with a minimum loss of coating build per pass. These coatings were manufactured in commercial facilities and test results obtained from these materials correlated with laboratory experimental data. Materials and application techniques developed as a result of this program have significantly reduced the costs of applying fastener-countersink seals to production aircraft. As a result of this and earlier programs, materials and application techniques developed have been adopted by the customer for use in sealing of critical areas susceptible to exfoliation corrosion on the A7 light attack aircraft currently being manufactured at Vought Aeronautics Corporation.</p>			

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Silicone elastomers						
Fastener sealing						

VOUGHT AERONAUTICS COMPANY

DEVELOPMENT OF FASTENER COUNTERSINK CORROSION PROTECTION SEALS

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## FOREWORD

The Fastener Countersink Protection Research Program was initiated in June 1967, under Naval Air Systems Contract N00019-67-C-0530 Phase I and continued under Naval Air Systems Command Follow-On Contract N00019-69-C-0132 Phase II. Completion of this third segment of this project (Phase III), also under Naval Air Systems Command per Contract N00019-70-C-0244, has brought this project to the present state-of-the-art. This project was administered as were the former contracts, by Tom Johnston of the Material Acquisition Group of the Engineering Division of Naval Air Systems Command. The object of this program was to study, develop and optimize elastomeric coating materials giving special emphasis to specific application techniques to materials developed for use in sealing fastener countersink heads within the critical areas of aircraft skins to prevent moisture ingress and subsequent exfoliation corrosion of this parts.

This program, as most present-day research programs, has been dependent on the cooperative efforts of individuals from a number of areas. Mr. Al Malloy of the Naval Air Systems Command has guided the investigation towards promising new elastomers and steered the program around potential pitfalls. Mr. S. Kaplan and S. Goldberg have provided insight into parameters to be studied in order to provide protection through the use of elastomers applied in coating thicknesses. Technical personnel within Vought Aeronautics and of material suppliers have been vital to the accomplishments of the program. Although the number precludes individual recognition, their efforts as well as those mentioned above are recognized and appreciated.

# ABSTRACT

The objects of this program were to modify coating materials for use with specialized application equipment, to study application techniques applicable to production practices and to develop a color stable (non-yellowing) material suitable for this use. All objectives were oriented toward development of an elastomeric sealant system designed for use in sealing fastener-head countersinks in highly loaded aircraft skins that are susceptible to exfoliation corrosion.

Materials were formulated that could be smoothly deposited on vertical surfaces to thicknesses of 5 to 7 mils per pass utilizing vapor-carrier type spray equipment; other materials formulated for use in conventional application equipment were easily applied to an aesthetically smooth finish with a minimum loss of coating build per pass. These coatings were manufactured in commercial facilities and test results obtained from these materials correlated with laboratory experimental data. Materials and application techniques developed as a result of this program have significantly reduced the costs of applying fastener-countersink seals to production aircraft. As a result of this and earlier programs, materials and application techniques developed have been adopted by the customer for use in sealing of critical areas susceptible to exfoliation corrosion on the A7 light attack aircraft currently being manufactured at Vought Aeronautics Corporation.

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## 1.0 INTRODUCTION AND SUMMARY

### 1.1 INTRODUCTION

This report describes a study and test program to supplement the Development of Fastener Countersink Protective Seals Program developed under Contracts N00019-67-C-0530 and N00019-69-C-0132. These initial programs have shown that elastomeric coatings are more resistant to cracking around highly loaded skin fastener heads in military aircraft than are the more brittle coatings. Materials such as polysulfides, silicones and elastomeric polyurethanes were selected for modification to improve the application characteristics of these coating materials without a loss of desirable characteristics. Work completed under Contract N00019-67-C-0530 has established the minimum theoretical coating thickness that need be applied to these aircraft structures in order to afford the desired degree of corrosion protection. Initial successes have lead investigators to modify coating materials developed earlier, fastener countersinks and material application techniques in order to develop a minimum weight-cost, aerodynamically smooth corrosion protective sealing system for fastener-head countersinks in highly loaded aircraft skins.

The problem is to prevent moisture from entering around fastener countersink heads causing subsequent exfoliation, spreading from the fastener head to the surrounding skin surfaces. If relatively brittle paint systems such as epoxies or non-flexible urethanes are used a number of concentric cracks is formed around each fastener head in these relatively brittle coatings. This crack formation is produced due to movement of the fastener heads during cyclic compressive-tension loading of these critical skin areas in flight. Operational temperatures around  $-65^{\circ}\text{F}$  renders these brittle materials more susceptible to cracking at these temperatures, since flexibility of these materials is reduced greatly at these temperatures.

In Phase II, test procedures were developed that simulate the flight loading and temperature conditions at which rupture occurs on aircraft paint systems around fastener heads. A test procedure too was designed to represent a typical upper wing skin fastener joint on the A7 aircraft; progressive load testing at  $-65^{\circ}\text{F}$  showed that the currently used brittle paint system would rupture and allow moisture intrusion at the fastener heads at approximately 80% of design limit skin stress. These test results lead investigators to select elastomeric materials for use in this sealing application. The most promising of the elastomeric materials were comparatively evaluated with current paint systems for sealing effectiveness. These materials were silicones, polysulfides, and elastomeric polyurethanes.

Silicone elastomers tested showed a tendency to lose adhesion after long term corrosion testing, and these materials lacked sufficient abrasion resistance for application to surfaces which would be subjected to foot traffic. Although the silicones exhibited a resistance to permeation of salt solution that is much higher than that of the polysulfides or of the polyurethanes, good adhesion and abrasion resistance were considered as criteria for selection of a material for optimization, and the silicones were rejected for further evaluation for use in this program.

The polysulfides were rejected for further evaluation by virtue of the poor abrasion resistance and poor resistance to salt water permeation exhibited by these materials.

The elastomeric polyurethanes proved to be highly abrasion resistant, resistant to salt water permeation and to adhere well to primed substrates. Weathering tests showed that these materials tend to yellow with age; therefore, these materials require a non-yellowing top coat if white is the desired color. A white top coat is also necessary with the silicones and polysulfides if a permanent white is desired. With this in mind at the beginning of Phase III, investigators selected the elastomeric polyurethanes for optimization.

## 1.2 SUMMARY OF PHASE III PROGRAM

A material of relatively high viscosity which contained a thixotropic agent was compounded to allow a high coating deposition rate per pass. This allowed the application of coatings ranging from 3 to 5 mils in thickness per pass that were free of sags and relatively smooth as compared to sprayable sealants. Innovations in application techniques were made by utilization of special spray equipment that employs a hot vapor carrier (TF Freon) for an atomization device. Use of this high viscosity material in conjunction with the vapor carrier spray equipment was instrumental in the development of a coating technique to cover specific areas to be coated without masking. A technique of coating fastener rows in close proximity to areas not requiring the coating was developed by producing a sprayed feather edge on the terminating edges of the coating strip. Perfection of this technique allowed overcoating of the sprayed strips with a finish enamel top coat, thus rendering the sealant strips completely oblivious through the top coat.

Aging tests begun in Phase II were terminated after 18 months weathering on the 80' atmospheric weathering lot at Kure Beach. Aging of other materials exposed to natural sunlight (southern roof exposure, Dallas Texas) was completed in order to determine the affects of weathering to the tensile strength and to the ultimate elongation of the elastomer.

Various aliphatic diisocyanates were compounded with suitable crosslinking agents to produce a non-yellowing material without loss of desirable characteristics developed earlier in former compounds. Compounds produced were non-yellowing, but cured too slowly for application without a baking facility to facilitate curing of these mildly reactive compounds.

A development study was completed for flexible primers for use with the elastomer. Commercially available primers were evaluated and a number of primers were synthesized. These primers were evaluated for flexibility at low temperatures and for resistance to salt spray and impact resistance.

Application of materials to fleet aircraft was begun in Phase II. These aircraft (F8's) were inspected by VAC Field Engineering personnel.

## 2.0 TEST PROCEDURES

### 2.1 CORROSION TESTS

Test specimens were fabricated of 7075-T6 bare aluminum alloy as described in Figure 1. This specimen design was chosen because alternate loading of these specimens under tension and compression simulates fastener head movement in highly stressed areas of the aircraft.

Specimens received corrosion preventative treatments as outlined in Table I. These treatments included the more promising techniques for corrosion protection of fasteners that are currently being used in the industry or being studied by other investigators. Specimens were fabricated per Figure 1 and coated per Table I. The even numbered specimens were loaded to 4400 lbs tension and 2000 lbs compression at a loading rate of 10 inches/minute for 205 cycles at -65°F. The specimens were examined for ruptures in the coating using a 10X binocular microscope and electrical conductive tests consisting of a salt water saturated cotton swab connected to a volt-ohm meter. Microruptures were detected by a change in resistance.

After fatigue cycling at -65°F, the even numbered specimens of Table I were exposed at the eighty foot atmospheric lot at Kure Beach for a total of 18 months.\*

Salt spray tests were conducted per Federal Test Standard 141-6061 (5% Na Cl fog) for primer evaluation.

### 2.2 IONIC PERMEABILITY

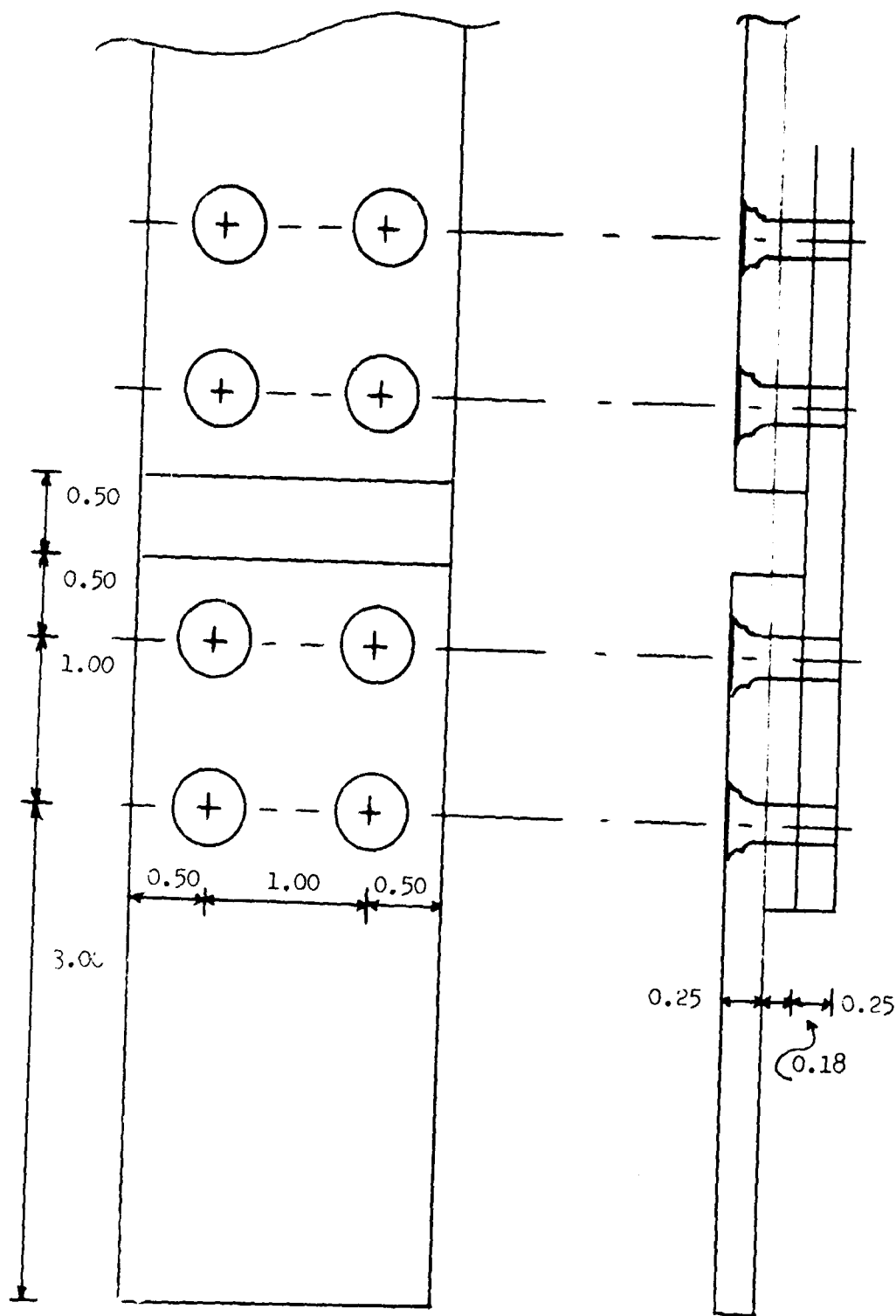
The ionic permeability of a number of polyurethane elastomers was determined by measuring changes in the capacitance of the coatings. The coatings were applied with their primers on 2024-O aluminum alloy test panels which had been chromic acid anodized. Parallel circular plate condensers were formed by bonding 2 inch lengths of 1.5 inch inside diameter acrylic tubing to the coated test panels, filling with a 3% salt water solution, and inserting a disc electrode 1.5 inches from the coating surface. The capacitance was measured immediately after filling the cells with salt water. Subsequent readings were taken periodically thereafter depending on the rate of capacitance change being experienced.

Capacitance of a circular parallel plate condenser can be expressed as the following:

$$C = k \frac{S}{4t}$$

where C = capacitance  
S = areas of the plate  
k = dielectric constant  
t = separation of the plates

\* Work begun in Phase II Contract N00019-69-C-0132.



Material: 7075-T6 Al Bare Countersink: CW 3037-4 Fastener: NAS 1624-11

FIGURE 1 CORROSION TEST SPECIMEN

TABLE I CORROSION TEST SPECIMEN PREPARATION

Specimen Number	Substrate Surface Preparation	Coating	Fastener Countersink Configuration	Fastener Coating	Fastener Installation Material (5)
11, 12	Sulfuric Acid Anodized	Polyurethane(1)	Radiused(4)	0.0002 In. Cadmium	None
13, 14	Sulfuric Acid Anodized	Polyurethane	Radiused	0.0003 In. Cd	None
15, 16	Sulfuric Acid Anodized	Polyurethane	Radiused	0.0003 In. Aluminum	None
17, 18	Sulfuric Acid Anodized	Polyurethane	Standard	0.0002 In. Cd	None
19, 20	Sulfuric Acid Anodized	Polyurethane	Standard	0.0003 In. Cd	None
21, 22	Sulfuric Acid Anodized	Polyurethane	Standard	0.0003 In. Al	None
23, 24	Sulfuric Acid Anodized	Polysulfide(2)	Radiused	0.0002 In. Cd	None
25, 26	Sulfuric Acid Anodized	Polysulfide	Radiused	0.0003 In. Cd	None
27, 28	Sulfuric Acid Anodized	Polysulfide	Radiused	0.0003 In. Al	None
29, 30	Sulfuric Acid Anodized	Silicone(3)	Radiused	0.0002 In. Cd	None
31, 32	Sulfuric Acid Anodized	Silicone	Radiused	0.0003 In. Cd	None
33, 34	Sulfuric Acid Anodized	Silicone	Radiused	0.0003 In. Al	None
35, 36	Chromic Acid Anodized	Polyurethane	Radiused	0.0002 In. Cd	None
37, 38	Chromic Acid Anodized	Polyurethane	Radiused	0.0003 In. Cd	None
39, 40	Chromic Acid Anodized	Polyurethane	Radiused	0.0003 In. Al	None
41, 42	Chromic Acid Anodized	Polyurethane	Standard	0.0002 In. Cd	None
43, 44	Chromic Acid Anodized	Polyurethane	Standard	0.0003 In. Cd	None
45, 46	Chromic Acid Anodized	Polyurethane	Standard	0.0003 In. Al	None
47, 48	Chromic Acid Anodized	Polyurethane	Radiused	0.0002 In. Cd	None
49, 50	Phosphate Chromate(6)	Polyurethane	Radiused	0.0003 In. Cd	None
51, 52	Phosphate Chromate	Polyurethane	Radiused	0.0003 In. Al	None
53, 54	Phosphate Chromate	Polyurethane	Standard	0.0002 In. Cd	None
55, 56	Phosphate Chromate	Polyurethane	Standard	0.0003 In. Cd	None
57, 58	Phosphate Chromate	Polyurethane	Standard	0.0003 In. Al	None
59, 60	Phosphate Chromate	Polyurethane	Standard	0.0003 In. Cd	None
61, 62	Phosphate Chromate	Silicone	Radiused	0.0002 In. Cd	None
63, 64	Phosphate Chromate	Silicone	Radiused	0.0003 In. Cd	None
65, 66	Sulfuric Acid Anodized	Polyurethane	Radiused	0.0003 In. Al	None
67, 68	Sulfuric Acid Anodized	Silicone	Radiused	0.0002 In. Cd	Mil-S-8802
			Fadiused	0.0002 In. Cd	Mil-S-8802



TABLE I (CONTINUED)

Specimen Number	Substrate Surface Preparation	Coating	Fastener Countersink Configuration	Fastener Coating	Fastener Installation Material (5)
69, 70	Sulfuric Acid Anodized	Polyurethane	Radiused	0.0002 In. Cd	Zinc Chromate Primer
71, 72	Sulfuric Acid Anodized	Silicone	Radiused	0.0002 In. Cd	Zinc Chromate Primer
73, 74	Sulfuric Acid Anodized	Polyurethane	Radiused	0.0003 In. Cd	Zinc Chromate Primer
75, 76	Sulfuric Acid Anodized	Silicone	Radiused	0.0003 In. Cd	Zinc Chromate Primer
77, 78	Sulfuric Acid Anodized	Polyurethane	Radiused	0.0003 In. Al	Zinc Chromate Primer
79, 80	Sulfuric Acid Anodized	Silicone	Radiused	0.0003 In. Al	Zinc Chromate Primer
81, 82	Sulfuric Acid Anodized	Polyurethane	Radiused	0.0002 In. Cd	Encapsulated Primer
83, 84	Sulfuric Acid Anodized	Silicone	Radiused	0.0002 In. Cd	Encapsulated Primer

(1) Polyurethane was applied over Epoxy Polyamide Primer, Mil-P-23377B (Polyurethane is material code 16)

(2) Polysulfide was applied over Epoxy Polyamide Primer, Mil-P-23377B (Polysulfide is material code 17).

(3) Silicone was applied over Silicone Primer (Silicone is material code 18).

(4) Ream radiused with an abrasive wheel modified to ream type tool configuration (material code 19).

(5) Materials used to coat fastener prior to assembly of specimens.

(6) See material code 19.

In this particular case  $k$  is the dielectric constant of the coating and  $t_0$  is the thickness of the coating. As electrolyte diffuses into the coating,  $t$  becomes the "unpenetrated film thickness". The term  $t$ , "unpenetrated film thickness" is theoretical and exists only by definition, since the electrolyte does not diffuse uniformly throughout the coating. It is a function of pore space in the coating into which electrolyte has to diffuse. The depth and frequency of these pores vary so that the concentration gradient of electrolyte penetration varies directly with that pore density.

The value  $t$  is determined in the following manner:

The equation for a circular parallel plate condenser is rearranged after substituting constants.

$$K = \frac{C_0 t_0}{(0.0885) S} \quad (1)$$

where  $S$  = area of the plate  
 $C_0$  = initial capacitance  
 $t_0$  = original film thickness

$$t = K \left( \frac{0.0885}{C} \right) S \quad (2)$$

where  $C$  = capacitance at any time  
 $t$  = "unpenetrated film thickness" at any time

If one substitutes equation 1 into equation 2 then

$$t = \frac{(C_0 t_0)}{(0.0885)S} \left( \frac{(0.0885)S}{C} \right)$$

$$t = \frac{C_0}{C} t_0$$

$t_0$  is measured with a thickness gage

$t$  is calculated from the ratio of initial and subsequent capacitance measurements.

## 2.3 FORMULATION OF VAD POLYURETHANES

The VAD polyurethanes were formulated according to Table II. A stoneware grinding mill jar with carborundum grinding media was used. The mill jar was dried at 160°F for 45 minutes, purged with dry nitrogen gas, and then charged with the component B raw materials shown in Table II. The mixture was milled until a fineness of grind value of 7 on the North Standard was reached. The milled base component was stored in lined quart cans which had been purged with dry nitrogen.

TABLE II  
MATERIAL FORMULATION PROPORTIONS

Compound I.D.	Basic Resin %	Crosslinking Agent - %	Catalyst %	Solvent %	Remarks
DPA#1	LL67-63.5	MOCA- 3.5	0.0	MEK-6.7 Toluene 11.6	Viscous requires zicon spray equipment to spray. HSI designation for test specimens.*
UJ#2	XP-57-28-84.1	MOCA-15.9	0.0	0.0	To viscous to brush, cures too slowly
UJ#3	XP-57-28-70.5	MOCA 13.3	0.0	MEK-16.1	Brushable viscosity cures too slowly
UJ#4	XP-57-28-60.0	MOCA-11.0	14491-0.5	MEK 28.5	Almost sprayable reacts too slowly at R.T. cures nicely at 140°F
UJ#5	XP-57-28-60.0	MOCA-11.0	14492-0.5	MEK-28.5	Same as UJ#4, except cure rate slightly faster
UJ#6	XP-57-28-60	MOCA-11.0	DABCO-0.5	MEK-28.5	Cures more slowly than UJ#4
UJ#7	XP-57-28-60	MOCA-11.0 MDA - 0.5	0.0	MEK-28.5	Slow cure rate
UJ#8	XP-57-28-60	MOCA-9.6 MDA - 1.9	0.0	MEK-28.5	Slow cure rate
UJ#9	XP-57-28-62	MOCA-5.8 MDA-2.9	0.0	MEK-29.1	Slow cure rate
DP#10	LD-2699-25.4	R-4SHT-37.3	FOMREZ-C2-0.5	MEK-37.3	Slow cure rate

\* Indicates materials compounded with pigments and fillers. Fillers and pigments used are described in Table II of Report N00019-69-C-0132.

TABLE II  
(Continued)

Compound I.D.	Basic Resin %	Crosslinking Agent - %	Catalyst %	Solvent %	Remarks
DP#11	LI67-65.2	MOCA-5.22	0.0	Acetone- 15.9	Sprays well, cures at room temperature well - MSB test specimen reference *
DP#12	LD-2699-26.0	R-45M-37.0	FOMREZ-C2-0.5	MIBK-37.0	Cure rate slow
DP#13	LD-2699-23.7	CS-15-37.5	FOMREZ-C2-0.5	MIBK-37.5	Cures too slowly for use
DP#14	LD-2699-23.7	CN-15-38.2	FOMREZ-C2-0.5	MIBK-38.2	Colorless polymer, cure rate too slow
DP#15	LD-2699-25.4	R-45HT-37.3	DABCO-0.5	MEK-37.3	Slow cure rate
DP#16	LD-2699-26.0	R45M-37.0	DABCO-0.5	MEK-37.5	Slow cure rate
DPA#17	LI67-60.0	MOCA-3.7	0.0	MEK-24.3	Material sprays with conventional spray equipment. MSA test specimen reference *
DP#18	LD-2699-25.0	CS-15-37.5	DABCO-0.5	MEK-37.5	Cures too slowly
DP#19	LD-2699-23.7	CN-15-38.2	DABCO-0.5	MEK-38.5	Slow cure rate
DPA#20	LI67-67.4	MOCA-3.7	0.0	Acetone 16.9	Cures well, icon spray equipment required for this coating application. HSLM test specimen reference *
UJ#21	UJ57-28 44.2	D-510 26.85	FOMREZ C2 0.42	MEK 28.40	Cures too slowly at room temperature
UJ#22	UJ57-28 44.2	D-510 26.85	FOMREZ C4 0.42	MEK 28.40	Cures too slowly at room temperature

TABLE II  
(Continued)

Compound I.D.	Basic Resin %	Crosslinking Agent - %	Catalyst %	Solvent %	Remarks
DP#23	L-2699 69.70	MDA-5.92 DETA - 0.354	0.0	MEK -11.82 Toluene- 11.82	Cures but, too slowly at room temperature
DP#24	L-2699 70.00	MDA-5.90 DETA-0.495	0.0	MEK-11.81 Toluene- 11.81	Cures to rubbery condition in less than 24 hours. Needs more solvent to spray well.
DP#25	L-2699 57.80	MDA-4.87 DETA-0.409	0.0	MEK-37.00	Addition of the DETA produced instantaneous gelation. Gelation is probably due to absence of toluene.
DP#26	L-2699 57.95	MDA-5.00	0.0	MEK-37.15	Material cured nicely to a rubbery condition in less than 16 hours at room temperature
DP#27	L-2699 60.00	MDA-3.20 DETA-0.15	0.0	MEK-36.62	Cure approximately same as DP#22. Aging tests begun for this material.

\* Indicates materials compounded with pigments and fillers. Fillers and pigments used are described  
in Table II of Report N00019-69-C-0132.

Component A was prepared by dissolving the solid materials shown in Table II in their respective solvents. The solvents were urethane grade and all cans were purged with dry nitrogen.

#### 2.4 ELONGATION AND TENSILE TESTS OF VAD POLYURETHANES

Free films were made for indicated formulations shown in Table II. Each formulation of polyurethane was applied to a mylar panel with suitable spray equipment. Five to ten coats of each formulation were applied in order to obtain approximately 20 mil thick films. After 30 days cure, dumbbell specimens were cut from the free films using die III shown in method 4111 of Federal Test Method Standard #601. Specimens were tested at room temperature using a TTD Floor Model Instron at a crosshead speed of 20 inches/minute, and at -65°F using a crosshead speed of 2 inches/minutes. Shore "A" hardnesses were also determined per Federal Test Method Standard #601, method 3021.

#### 2.5 DRYING TIMES OF VAD POLYURETHANES

Each formulation of polyurethane shown in Table II was applied over MIL-P-23377B primer to a total film thickness of approximately 1.5 mils. Both tack free and dry hard drying times were determined per Federal Test Method Standard 141 method 4061.

#### 2.6 SUNLIGHT EXPOSURE

The free films described in Section 2.4, test procedure for elongation and tensile tests, were also exposed to sunlight for weathering tests. The free films were placed on racks having Southern exposure at a 45° angle.

#### 2.7 VISCOSITY DETERMINATION METHODS

Viscosity data for all elastomers compounded at VAC listed in Table II were determined per Federal Test Standard 141 Method 4282, except as noted.

#### 2.8 FLEXIBILITY TEST PROCEDURE

Coating flexibility was determined for selected elastomers and flexible primers using 6.0 in. by 7.0 in. aluminum alloy test panels on a conical mandrel bend test per Federal Test Standard 141-6221. Tests were performed at room temperature and at -65°F. Impact tests were performed using a 5/8 in. diameter hemispherical falling punch. Impact tests were performed at 40 inch-pounds in most cases. Impact tests were performed exclusively at room temperature.

#### 2.9 FLIGHT TEST PROCEDURE\*

The polyurethane (material code 16), polysulfide (material code 17) and silicone (material code 18) were applied to the upper wing fold area of an F-8 aircraft using conventional spray equipment. The coatings were applied

\* This application procedure was utilized in Phase II Contract N00019-69-C-0132.

as thin as possible while providing coverage of conventional countersinks. Then the coatings were applied approximately 1.0 mil thicker in areas adjacent to the areas of minimum thickness. The resulting thicknesses were 5.5 mils and 6.5 mils for the polyurethane, 2.2 mils and 3.3 mils for the polysulfide and 1.3 mils and 2.3 mils for the silicone coating. These areas were checked periodically for radial cracks around the fastener heads using a 10 power magnifying glass or electrically using volt-ohm meter and probe saturated with a sodium chloride salt solution.

The VAD M-9 polyurethane was applied to the upper left unit horizontal tail of three RF-8G aircraft. Table III gives the application procedure and aircraft bureau numbers.

2.9.1 Detailed Coating Application Procedure for F8 Aircraft Coated In Phase II

TABLE III

APPLICATION PROCEDURE FOR FLIGHT TESTING VAD POLYURETHANE ELASTOMERS

Bureau Number	Application Procedure
	(1) Upper surface of left unit horizontal tail was hand wiped with a solvent cleaner and abrasive pad (material code 8)
	(2) Steam cleaned.
	(3) Treated with a MIL-C-5541 Chromate Chemical film
146861	(4) MIL-P-23377 B Epoxy Polyamide Primer was applied
	(5) A mist coat of VAD M-9 polyurethane was applied over the primer after a 20 minute drying time.
	(6) After waiting 10 minutes a full coat of M-9 was applied. A second full coat was applied 45 minutes later.
	(7) A non-yellowing linear polyurethane topcoat was applied 1.0 hours after the final coat of M-9. (See material code 27 LP-4) Both the primer and the linear polyurethane were applied using a conventional pressure pot. The M-9 elastomer was thinned 50% with methyl ethyl ketone and applied with airless electrostatic spray equipment. The temperature was 75°F and relative humidity was 44% during the application.
	(1) Upper surface of left unit horizontal tail was hand wiped with a solvent cleaner and abrasive pad (material code 8)
144613	(2) Steam cleaned.

TABLE III

Bureau Number	Application Procedure
144613	(3) Treated with a MIL-C-5541 chromate chemical film
	(4) MIL-P-23377B Epoxy Polyamide Primer was applied
	(5) A mist coat of VAD M-9 polyurethane elastomer was applied over the primer after a 1 hour drying time
	(6) After waiting 30 minutes a full cross coat of M-9 was applied over the structural fasteners only
	(7) A linear polyurethane topcoat (material code 27 LP-4) was applied over the M-9 elastomer prior to delivery of the aircraft to the Navy. A conventional pressure pot was used to apply all the coatings. M-9 was not thinned. The temperature was 79°F and relative humidity was 40% during the application.
146845	(1) Upper surface of left unit horizontal tail was wiped with a solvent cleaner and abrasive pad (material code 8)
	(2) Solvent wiped with methyl ethyl ketone and cheese cloth
	(3) Treated with a MIL-C-5541 chromate chemical film
	(4) MIL-P-23377B Epoxy Polyamide Primer was applied
	(5) Primer was allowed to dry 40 minutes then a mist coat of M-9 was applied.
	(6) After 15 minutes a full coat of M-9 was applied
	(7) After 1.5 hours a second full coat of M-9 was applied
	(8) A linear non-yellowing top coat (material code 27 LP-4) was applied over the M-9 elastomer prior to delivery of the aircraft to the Navy.
All coatings were applied using a conventional pressure pot. The temperature was 73°F and the relative humidity was 28% during the application.	



## 2.10 COATING APPLICATION TECHNIQUES SPECIALIZED EQUIPMENT

Coatings containing a high percentage of solids were deposited on test panels, mylar films (for free film sheets) and to scrapped aircraft assemblies utilizing vapor carrier application equipment. See paragraph 2.10.1 for a description of this equipment manufactured by Zicon Chemtronics. Surfaces to be coated were cleaned with solvents and or paint strippers, then abraded with scouring pads (material code 28 ) and a special cleaner (material code 29 ) to absorb any residual oil that might be left around fastener heads. The surface was then abraded lightly with abrasive pads and blown clean with oil free compressed air. A water break test was then applied to determine if surface to be coated was free of contaminants. A chromate chemical treatment was then applied on the surface to be painted. Primer was applied and allowed 15-30 minutes drying time before application of the first coating. The Zicon unit was regulated to provide a chemsine vapor pressure of 45 to 50 psig and an exit temperature of the chemsine vapor (atomizing agent) of approximately 140°F. A light mist coat of the coating was applied 0.8 to 1.5 mils in thickness. Approximately five minutes were allowed for escape of solvents before application of a full spray pass giving a total film thickness of approximately 4.0 to 5.0 mils. Another fifteen to thirty minutes time period was allowed for solvents to escape before application of subsequent coats of the elastomer etc. until the desired film thickness was attained.

### 2.10.1 Zicon Vapor Carrier System

In the Vapor Carrier System, the atomizing agent is a pure warm, dry, clean hydrocarbon vapor -- such as Zicon's Chemsine\*, which has three times the molecular weight of air. This heavy vapor produced finer atomization of the coating material at pressures as low as 2 psi than does air at much higher pressures. Because the vapor is free from water, oil, dirt, or other contaminants, and because it is chemically inert to the coating material (i.e. will not react chemically with it or its solvent) it cannot cause undesirable modification of the material.

The low velocity and pressure at which the coating material is conveyed by the vapor to the target surface minimizes overspray or bounceback. As the vapor leaves the gun, it contracts, effectively confining the spray and concentrating it in a uniformly predictable and controllable vapor "fan". This saturated vapor fan ensures that the levelling agents and liquifiers in the coating formulation are held in the best possible contact with and concentration at, the surface to be coated.

The heat energy in the vapor is then of significant assistance in speeding the evaporation of solvent from the coated surface. The resultant coating is remarkably uniform, pinhole free, and perfectly bonded to the target surface.

\* See appendix for Zicon specifications and flow schematic.

### 3.0 TEST RESULTS

#### 3.1 RESULTS OF EXTENDED WEATHERING TESTS: (Task I)

##### 3.1.1 Natural Weathering Sunlight Aging

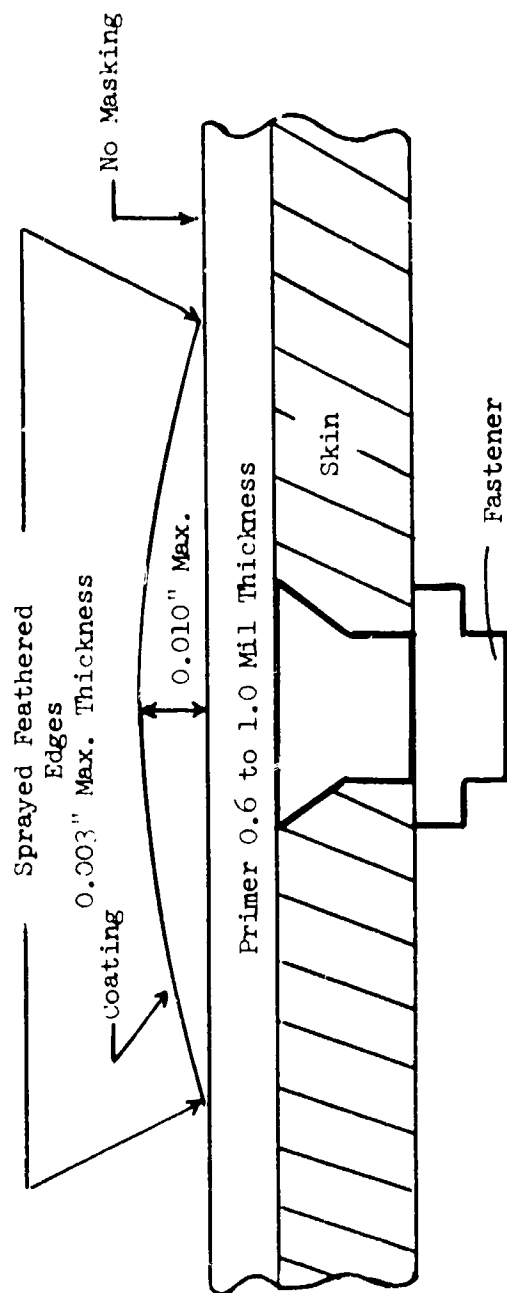
Aging specimens exposed to natural weathering on roof top racks, inclined 45° to the horizontal, with a southern exposure showed only slight degradation of ultimate tensile strength and ultimate elongation. These values were determined after exposure of free films of various formulations of the elastomer for 90 days. These data were compiled in Table IV.

##### 3.1.2 Atmospheric Corrosion Tests - Kure Beach

Rupture fatigue specimens exposed to atmosphere weathering on the 80' lot at Kure Beach were photographed. Figure 3 is a photograph of these low temperature rupture fatigue specimens exposed eighteen months in this test. Specimens numbers 16, 26, and 32 are polyurethane M3 formulation, polysulfide material code 17 and silicone material code 18 respectively. Aberrations produced in these specimens are indicated by the black pointers on each specimen except in the case of the polysulfide specimen that was uniformly crazed. The black pointer on specimen 26 of Figure 3 shows the mechanical damage that occurred frequently in specimens coated with polysulfide (material code 17). Specimen number 32 of Figure 3 shows the ease with which the silicone (material code 17) can be broken; the black pointer indicates a break made by slight fingernail pressure. Figure 4 is a photograph of specimens coated with polyurethane (material code 17) showing corrosion sites around fastener heads (black pointer). Corrosion sites of this type were not typical in these specimens and only occurred in this coating in approximately two percent of the fasteners. Although crazing had occurred in the polyurethane coating, this material was affected less adversely due to weathering than were the other materials tested. Table V describes the condition of these specimens.

#### 3.2. RESULTS OF SPECIAL APPLICATION EQUIPMENT EVALUATION (Task II)

Laboratory size aluminum alloy test panels were coated with the vapor-carrier type spray equipment. Simulated fastener countersink patterns were coated in laboratory quite effectively with this unit. Coatings deposited cured to a relatively smooth finish as compared to sealants of this type sprayed with conventional air dispersed spray equipment. Aircraft assemblies were coated utilizing the vapor-carrier spray equipment successfully. Good results were obtained utilizing a narrow spray pattern to coat individual rows of fasteners that were not masked. Rows sprayed with a feather edge were easily overcoated without hand sanding or fairing of these strips prior to overcoating. Figure 2 was included to depict a cross section of a typical coating strip over fastener heads. Figures 5 and 6 are photographs of various aircraft assemblies coated with the Zicon spray equipment. Application equipment specifications were outlined in tabular form in Appendix I, Table I. Table II of the Appendix outlines recommended coating viscosity range to be used with the Zicon spray equipment.



X-Section through a typical coating strip applied over fastener heads - no masking used

FIGURE 2 SCHEMATIC OF A TYPICAL FEATHER-EDGED STRIP NO MASKING UTILIZED

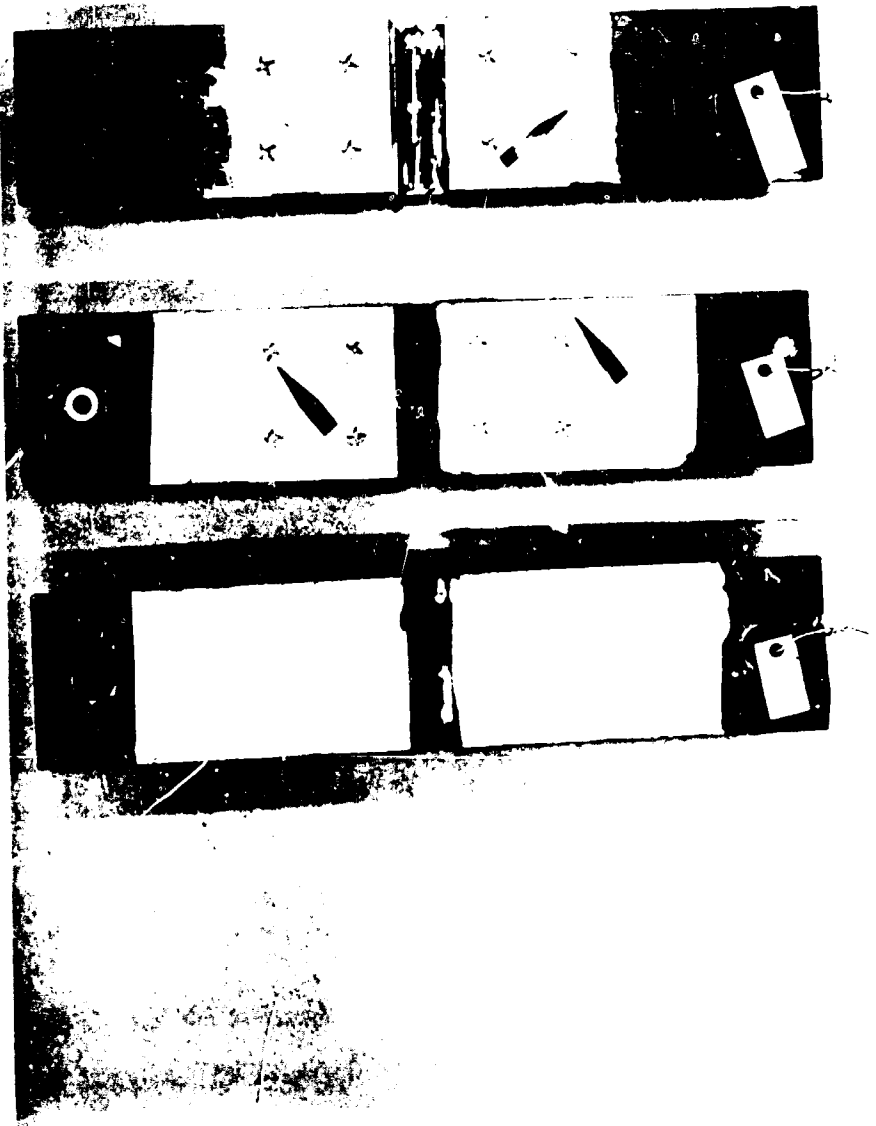


FIGURE 3 LOW-TEMPERATURE RUPTURE FATIGUE SPECIMENS EXPOSED 18 MO. AT KURE BEACH; #16 IS M9 ELASTOMERIC POLYURETHANE CONDITION AFTER TEST-CRAZED, #26 IS POLYSULFIDE CONDITION AFTER TEST - MECHANICAL DAMAGE - SEE POINTER, #32 IS SILICONE CONDITION AFTER TEST - LOSS OF ADHESION - SEE POINTER

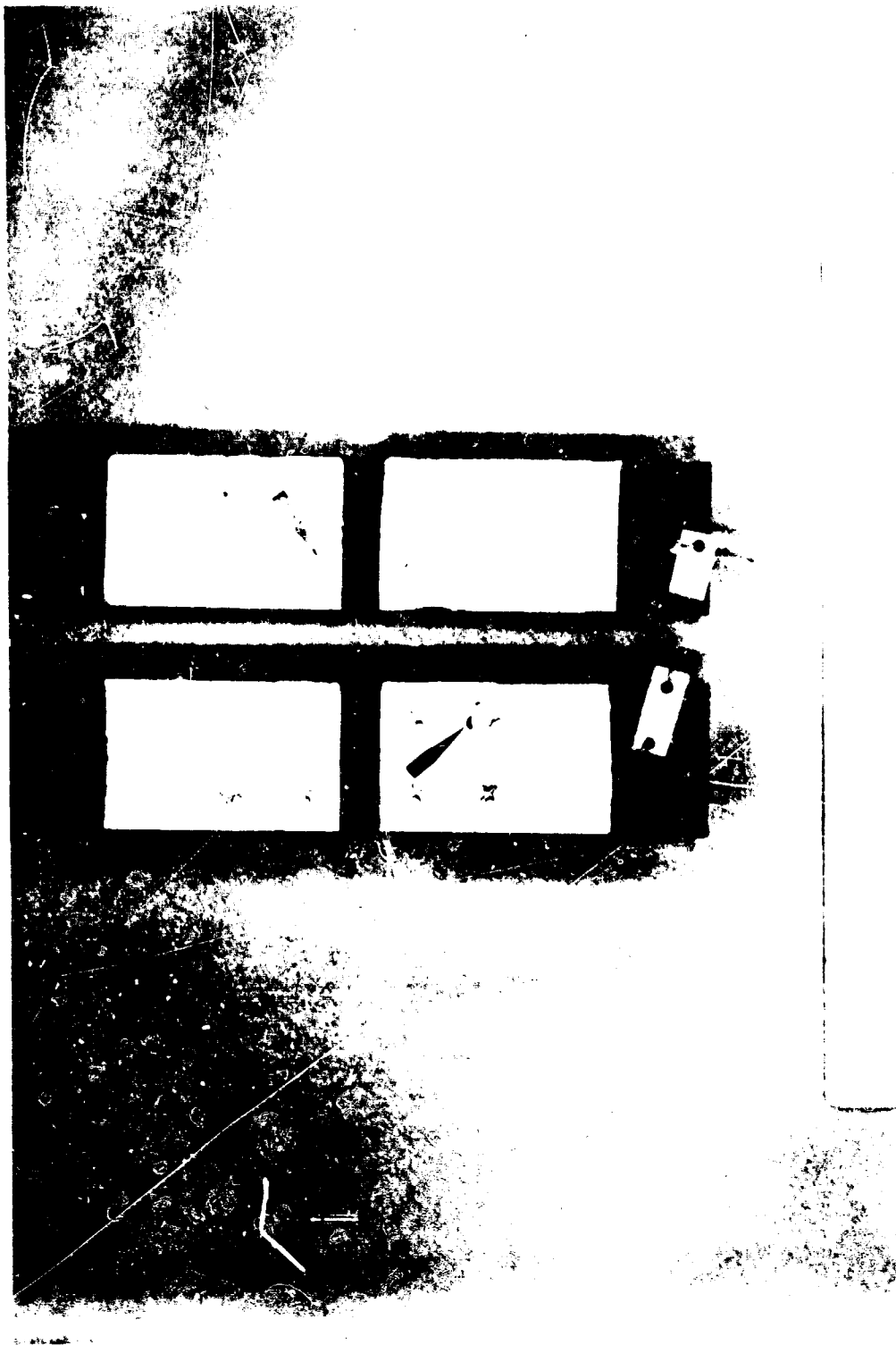
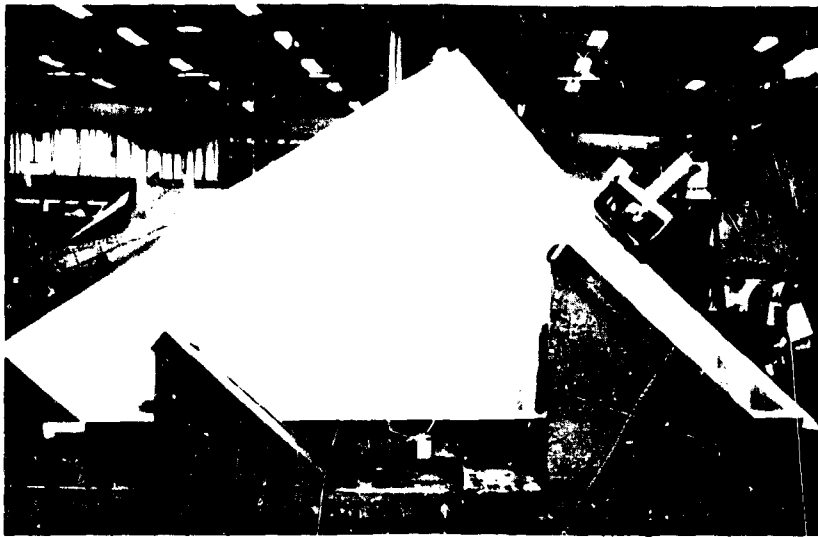


FIGURE 4 LOW-TEMPERATURE FATIGUE SPECIMENS EXPOSED 18 MO. AT KURE BEACH, BOTH SPECIMENS ARE M9 ELASTOMERIC POLYURETHANE, CONDITION AFTER TEST - CORROSION AROUND FASTENER HEAD - SEE POINTER



Unit Horizontal Tail Coated with HSI Polyurethane  
No Masking of Fastener Rows - Coating Thickness 5-7 mils  
Applied with Vapor-Carrier Spray Equipment

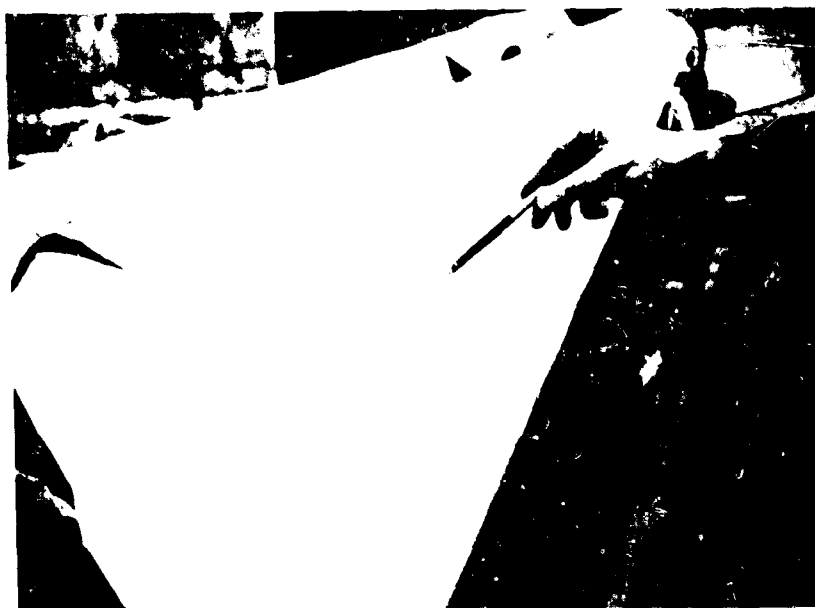


Close Up Showing Coated Fasteners in Main Torque Box  
of UHT in A-7E Aircraft - Coating Thickness 5-7 mils

FIGURE 5 AIRCRAFT ASSEMBLIES COATED WITH VAPOR-CARRIER  
SPRAY EQUIPMENT - NICON EVALUATION



Close Up Showing Coated Fasteners in Main Wing  
Center Section A-7E Aircraft - No Masking Utilized  
Polyurethane Overcoated Coating Thickness 5-7 mils



Close Up of Assembly Coated by Strip Technique  
Grey Areas are Primer - White Polyurethane  
No Masking Used Coating Thickness 4-6 mils

FIGURE 6 AIRCRAFT ASSEMBLIES COATED WITH VAPOR-CARRIER  
SPRAY EQUIPMENT - ZICON EVALUATION

TABLE IV MATERIAL PROPERTIES BEFORE AND AFTER SUNLIGHT AGING (3)

Formulation*	Average Room Temp. Elongation %		Average Room Temp. Tensile Strength (psi)		Average Elongation at -65°F (units %)		Average Tensile Strength at -65°F (psi)	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
M-1	463	473	521	1065	184	177	7,561	8,561
M-2	560	595	526	1376	207	210	8,999	10,050
M-3	328	463	507	1066	183	176	9,028	8,744
M-4	397	437	467	865	146	130	7,304	7,073
M-7	443	430	3,159	5265	180	137	10,412	8,756
M-8	440	380	3,739	4711	168	115	9,122	9,230
M-9	393	333	2,812	319	223	107	12,313	3,468
M-9A	373	383	2,927	5326	203	113	11,179	8,591
M-9B	423	473	3,402	5022	193	117	11,505	9,232
M-10	420	497	2,010	3758	198	147	10,194	8,900
Light Gull Grey	463	460	2,680	3015	10%	10%	5,920	8,400
AML P-7	630	535	2,090	2646	253	150	8,680	8,387
Oiln #6559(1)290	--	--	6,676	--	163	--	--	10,109
Oiln #6564(2)30	--	--	188	--	187	--	--	7,030
Oiln #6572(1)336	--	--	3,900	--	230	--	--	9,903

(1) Aged specimen reverted

(2) Aged specimen too brittle to test

(3) Specimens aged approximately 90 days in natural sunlight.

\* Formulations are same as defined for Contract No. N00019-69-C-0132, Table II, page 10.



TABLE V EFFECTS OF WEATHERING TO LOW-TEMP. RUPTURE-FATIGUE SPECIMENS (18 Nos. Fire Beach)

Specimen No.	Material Code	Deflects Observed - Actual Count					Abrasions
		Crazing	Hairline Cracks	Breaks	Exposed Edge of Fastener Head	Breaks in Torque Drive Slots Only	
12	16	Yes	-	1	4	-	-
14	16	Yes	-	-	3	-	-
16	16	Yes	-	1	1	-	-
18	16	Yes	-	-	2	5	-
20	16	Yes	-	2	4	-	-
22	16	Yes	1	2	3	-	-
24	17	-	-	-	-	2	6
26	17	-	-	-	-	6	9
28	17	-	-	-	-	3	1
30	18	-	-	1	1	-	1
32	18	-	-	1	1	-	1
34	16	Yes	-	-	-	-	3
36	16	Yes	2	2	1	2	-
38	16	Yes	-	-	2	7	-
40	15	Yes	1	-	6	3	-
42	16	Yes	-	-	4	-	-
44	16	Yes	2	5	-	3	-
46	16	Yes	3	2	-	3	-
48	16	Yes	-	6	-	-	-
50	16	Yes	1	-	1	-	-
52	16	Yes	4	-	7	-	-
54	16	Yes	4	3	5	-	-
56	16	Yes	5	4	5	-	-
58	16	Yes	-	7	-	-	-
60	18	Yes	1	2	-	-	-
62	18	-	-	-	-	-	3
64	18	-	-	-	3	1	-
66	16	-	3	3	1	6	-
68	18	-	4	1	-	4	-
70	16	Yes	1	7	-	5	-
72	18	-	-	6	-	-	-
74	16	Yes	5	2	-	-	4
76	18	-	1	3	-	-	-
78	16	Yes	1	5	9	-	-
80	18	-	1	1	2	-	-
82	16	Yes	1	6	-	3	-
84	18	-	-	-	-	-	-

### 3.3 RESULTS OF MATERIAL FORMULATION STUDIES (Task III)

#### 3.3.1 Non-Yellowing Formulation Task

A number of non-yellowing material formulations compounded failed to cure at room temperature, but cured to a tough resilient rubber at elevated temperatures. These compounds were rejected for compounding with pigments and fillers, since the need for an extensive equipment expenditure for baking equipment precluded any additional development of these formulations. A small number of materials compounded cured satisfactorily at room temperature for a practical coating application. These materials have remained color fast for approximately five months; however, when compounded with pigments and fillers, these materials also failed to cure at a rate satisfactory for suitable coatings application. Materials formulated were included in Table II.

#### 3.3.2 Material Formulation Optimization

Means by which the storage life of the material could be extended were explored. Samples of the thixotropic agent used in the formulation were found to contain an average of 3.5% (by wt) moisture. This moisture was driven off by firing of the thixotropic agent for two hours at 1000°F; after standing for a period of approximately twenty-four hours in a high-humidity environment, this material regained this moisture. Since the diisocyanate used in formulation of this elastomer is polymerized by the presence of free moisture, a decision was made by investigators to replace the hygroscopic thixotropic agent with one of a hydrophobic nature. A contact with one manufacturer of thixotropic agents indicated that a saline-treated material was available that was purported to be of a hydrophobic nature, it was later determined however that this was not available. Other materials received for use in this formulation were found to be hygroscopic; therefore, the decision was made to fire all thixotropic agents used in formulations just prior to addition of the material into the clean mill jar that had been purged with dry nitrogen gas during compounding. The stability of materials formulated using the fired thixotropic agent proved to be satisfactory. See service application study for results of stability tests of these compounds. In general, materials manufactured using dry solvents, fired thixotropic agents and stored only in containers that had been purged with dry nitrogen gas to exclude moisture laden air were quite stable, and these proved to be useable after as long as six month storage period.

#### 3.3.3 Materials Formulation Changes

3.3.3.1 Materials were formulated for use especially in the vapor carrier spray equipment (Zicon spray unit). This material formulation (designated HS-1) was used with the vapor carrier equipment to easily apply sag-free coatings on vertical surfaces that were 5 to 7 mils in thickness. The high viscosity and surface tension of this material would not permit the escape of all solvents before the "skin" on the partially cured coating formed, which resulted in a slight grainy appearance of the cured coating. Microscopic examination of sections cut through a cured free film of the coating showed the grainy surface appearance was due to very minute bubbles that had not broken the surface tension of the liquid coating before gelation of the material.

Tests proved that slow solvent release was partially responsible for this phenomenon.

3.3.3.2 Capacitance measurements were performed for samples of the HS-1 material that had been applied with the Zicon chemtronic spray equipment. The rate of salt water permeation was slightly higher for this material than for that of the M9 formulation applied with conventional spray equipment; however the film thickness of the HS-1 material tested was twice as thick as that of the M9 tested. The greater thickness of the film probably prevented escape of volatiles during the early stage of cure. This produced a slightly more porous material than that produced with the less viscous M9A formulation as evidenced by microscopic examination of edge sections of these films. Capacitance data were presented in Table VI.

3.3.3.3 Materials were compounded that were of a lower viscosity than the HS-1 and HS-1M formulas for use in conventional spray equipment. These compounds (identified as MSA and MSB) contained more solvent than the high viscosity compounds in order that these materials would spray adequately using the conventional equipment. Test panels coated with these compounds were smoother than those coated with the high solids (HS) series of materials. The loss of some build per pass was noted on spraying these formulations on vertical as compared to the HS compounds. Sag-free coatings were deposited on vertical surfaces utilizing these medium solids (MS) materials that ranged in dry film thicknesses from 3 to 5 mils. Application characteristics of these (MS) coatings were described in more detail in section 3.6. Table II was included to describe all material formulations compounding changes.

3.3.3.4 Free films of the elastomer made with the MSB formulation were easily built up to 75 mils in thickness dry film utilizing conventional suction cup spray equipment. Approximately 18 cross coat passes were required to accomplish this film thickness. Results of mechanical property tests were tabulated in Table VII.

3.3.4 Samples of the MSB medium solids elastomer that were overcoated and exposed to natural roof-top weathering showed no signs of adverse degradation. The MIL-C-81773 linear polyurethane top coat was still adhering to the elastomer after four months exposure or 45° inclined weathering racks at VAC in Dallas. The coating was adhering well to the elastomer even in areas that had been impacted with a 5/32" dia. hemispherical punch prior to weathering exposure tests. Some slight cracking of the MIL-C-81773 top coat was observed. No loss of flexibility had occurred in either the elastomeric polyurethane or the linear top coat at this age.

#### 3.4 FASTENER SEALING AS A DESIGN FUNCTION (Task IV)

Coated Fastener Countersinks - Removal, Reinstallation and Cycle Loading Tests - Coating the fastener countersinks before fastener installation was considered as a method of sealing countersinks in panels in which the fasteners must be removed frequently. A preliminary test was devised to determine the feasibility of this concept, (i.e. first to determine if damage to the coating material in the fastener countersinks occurs as a result of fastener

TABLE VI CAPACITANCE DATA - IONIC PERMEABILITY OF HS-1 ELASTOMER APPLIED USING ZICON CHEMTRONIC SPRAY EQUIPMENT

Time (hours) that a 3% NaCl solution is allowed to permeate the coating	HS-1 Polyurethane Elastomer applied over Mil-P-23377B Epoxy Polyamide Primer (total film thickness 7.5 mils)			Mil-C-22750 Epoxy Polyamide Enamel applied over HS-1 Polyurethane Elastomer over Mil-P-23377B Epoxy Polyamide Primer (total film thickness 7.5 mils)		
	Capacitance (nF)	Unpenetrated Film Thickness (mils)	Penetrated Film Thickness (mils)	Capacitance (nF)	Unpenetrated Film Thickness (mils)	Penetrated Film Thickness (mils)
0.0	0.31	7.50	0.00	0.44	7.50	6.00
1.0	0.41	5.65	1.85	0.49	6.73	0.67
1.5	0.43	5.40	2.10	0.49	6.35	1.15
2.1	0.46	5.05	2.45	0.52	6.00	1.50
3.0	0.49	4.74	2.66	0.55	5.68	1.82
3.2	0.49	4.74	2.66	0.58	5.50	2.00
5.4	0.49	4.74	2.66	0.60	5.50	2.00
6.3	0.49	4.74	2.66	0.60	5.40	2.10
7.0	0.53	4.38	3.12	0.61	5.24	2.26
24.0	0.53	4.38	3.12	0.63	5.24	2.26

PERMEABILITIES OF VARIOUS POLYURETHANE FORMULATIONS			
Coating Formulation	Coating Thickness (mils)	Maximum % Pore Saturation of a 3% NaCl Solution	
AML P-7(1)	3.0	32	
	3.8	37	
	5.5	31	
M-9A applied with Airless Electrostatic Spray Equipment	1.3	20	
	2.5	31	
	3.5	35	
HS-1 (2)	7.5	42	
HS-1 overcoated with Mil-C-22750 Epoxy Polyamide Enamel	7.5	30	

(1) Applied with conventional spray equipment  
(2) Applied with Zicon Chemtronic spray equipment

TABLE VII MECHANICAL PROPERTIES OF MSB COMPOUNDED AT  
VARIOUS STOICHIOMETRY RATIOS

Stoichiometry- % of Theoretical	Ultimate Tensile Strength psi		Percent Ultimate Elongation	
	Room Temperature Value	-65°F Value	Room Temperature Value	-65°F Value
60	9300	18200	815	129
85	9400	17500	865	149
90	8100	15400	738	104
95	5400	15700	708	84
100	4900	15000	517	79

installation.) No damage to the coating was noted after a number of installations and removals; therefore, specimens having coated fastener countersinks were assembled and torqued to specification after the coating cured. Specimens were cycle loaded at the rate of 10 inches per minute to 4800 pounds tension, then reversed to 3000 pounds compression. Specimens were subjected to a total of 200 loading cycles each at room temperature. The torque required to remove each fastener was recorded, and the difference in the before and after torque values was noted. Fastener torque was lost in all specimens tested, since loads stated above represent a 19% overload in tension and a 50% overload in compression; as expected; however, the fasteners in the coated countersinks lost torque to a greater extent than did the fasteners in the uncoated countersinks. A percent torque loss of 41, 66, 60 and 67 was noted for, radiused fastener-regular countersink, plain fastener-regular countersink, radiused fastener-coated countersink and plain fastener-coated countersink respectively. Specimens were disassembled and observed for damage to the coating beneath the fastener heads in the countersink. The coating beneath the fasteners having radiused heads seemed to be in better condition after loading and disassembly than that beneath the plain (i.e. non-radiused) fasteners. This was difficult to ascertain, because little damage to the coating was noted in the case of either type fastener and a relatively small number of specimens was tested in this test.

### 3.5 RESULTS OF FLEXIBLE PRIMER STUDY (Task V)

#### 3.5.1 Flexible Primer Development and Evaluation

Flexible primers formulated were listed in Table VIII. The epoxy polyamide materials compounded cured well, were sprayable, but lacked low-temperature flexibility. Epoxy-polyurethane materials formulated failed to cure satisfactorily. A polysulfide-polyurethane material primer formulation cured well, but failed to develop sufficient hardness and abrasion resistance.

##### a. Epoxy-Polyurethane Primer

Adiprene L100 was investigated as a flexibilizer for epoxy resin. Adiprene L100 and epoxy resins tend to undergo a slow thickening reaction when mixed. (Believed to be due to a reaction between isocyanate and hydroxyl groups). Therefore, a three component coating was made. Adiprene and epoxy Epon 828 resin were mixed in equal parts by weight. Then the following curing agents were tested with the resin blend:

- o MOCA, 4, 4' methylene, bis (2 chloroaniline)
- o MDA 4, 4' methylene dianiline
- o Phenylenediamine
- o Ring R-T-3 Curing Agent
- o Epon Curing Agent T
- o Epon Curing Agent B-1
- o Epon Curing Agent U

TABLE VIII CHARACTERISTICS OF FLEXIBLE PRIMERS FORMULATED

Material Type and Percentage Weight	Curing Agent	Cure Rate	Spray Characteristics	Comments
Epoxy-Polyurethane 828 I/100 50/50	MOCA (1)	Too slow. Tacky after 48 hours	Good	Reacts too slowly for practical application
"	MDA (3)	Too fast	N.T.	Reacts too rapidly for practical application
"	Phenylendiamine	"	"	"
"	Ring RT-1 Curing Agent	"	"	"
"	Epon Curing Agent T	"	"	"
"	Epon Curing Agent B-1	"	"	"
"	Epon Curing Agent U	"	"	"
Epoxy-polyamide 828/v140 50/50	Versamide 140	Cures tack free in 24 hours	Good - Diluted with 50/50 MEK/butyl cellosolve 1.3 Resin to 1.0 solvent/weight	Flexibility minimal
55/45	"	"	"	"
60/40	"	"	"	"
65/35	"	"	"	"

TABLE VIII (CONTINUED)

Material Type and Percentage Weight	Curing Agent	Cure Rate	Spray Characteristics	Comments
Epoxy-Polyamide 828-VI40 70/30	Versamide 140	Cures tack free after 72 hours	N.T.	Cure rate too slow
Epoxy-Polyamide 815-VI40 50/50	"	Cures tack free in 24 hours	"	"
Epoxy-Polyamide 815-VI40 55/45	"	"	Good - Diluted with 50/50 MEK/butyl cellosolve-50/50 resin to solvent by wgt.	Deposits a continuous coating. 7 mil to 1.0 mil thick. Flexibility minimal
Epoxy-Polyamide 815-VI40 60/40	"	"	"	"
Epoxy-Polyamide 815-VI40 65/35	"	Cures tack free in 48 hours	N.T.	Cure rate too slow for practical application
Epoxy-Polyamide 815-VI40 70/30	"	Cures tack free in 72 hours	"	"
Polysulfide-Polyurethane 50/50	Proprietary	Cures tack free in 12 hours	Good	Material failed to develop sufficient hardness and abrasion resistance

(1) MOCA = 4, 4', methylene, bis, 2-chloroaniline

(2) MDA = 4, 4' Methylene dianiline

(3) N.T. = Not Tested



MOCA was the only curing agent that could be used with the resin blend since all the other curing agents reacted too rapidly with the adiprene. However, MOCA reacts too slowly at room temperature with Epon 828 to make this system practical. Spray-outs of the MOCA cured resin were still tacky after 48 hours and the coating had not reached full cure after 6 days.

b. Epoxy-Polyamide

Epoxy resins and certain polyamides of high molecular weight polymerize, when reacted in a ratio of approximately 1 to 1 by weight, and produce a rigid, yet fairly flexible material. Changing the stoichiometry in either direction, within limits, tends to improve flexibility of the material. Epoxy-polyamide materials were thinned for spraying using solvents indicated in Table VIII. Cure rates of materials compounded were determined, and cured films were bend tested at -65°F per Federal Test Standard 141 Method #6222. Preliminary data indicated the epoxy-polyamide formulations tested lacked sufficient flexibility to be practical.

c. Polysulfide-Polyurethane

A mixture of polysulfide and polyurethane coatings was also investigated as a flexible primer.

A sprayable version of MIL-S-8802 was mixed in equal proportions with a polyester linked polyurethane enamel. The material sprayed well and reached a tack free state in 12 hours. However, the material was soft and had poor abrasion resistance after 5 days cure.

3.5.2 Evaluation of Commercial Flexible Primers

A number of commercially available flexible primers was selected for testing. These materials were polyurethanes, modified polyvinyl butyrals, modified epoxies, reactive silanes and some were proprietary formulations. Primers were subjected to preliminary screening tests, the results of which are presented in Table IX. Although primer systems #23, #24, and #26 successfully passed all tests defined in Table IX, these were rejected for additional tests, since these materials contained no pigment and were considered a poor risk for prevention of corrosion. System 22 failed the conical mandrel test at -65 ° and also the room-temperature impact test. Results from a thirty day salt spray test indicated that the control primer MIL-P-23377 Code #26 was slightly superior to other primers tested with respect to corrosion protection afforded to the substrate during salt spray exposure. Corrosion resistance primer data were tabulated in Table X, and primers were given a general rank (all substrate treatments considered), and each was given a specific rank for individual surface treatment. Test results for 180° Peel Strength Tests were reported in Table XI. These data indicate that the control MIL-P-23377 primer provides the best bond strength of the elastomers polyurethane to the substrates tested. Primer system #15 was second only to the control primer in this test as in the corrosion resistance test, clearly establishing this system as the second best material tested in this series of tests. Figures 7, 8, and 9 depict salt spray test specimens of these flexible primers tested.

TABLE IX FLEXIBLE PRIMER TEST DATA

Primer Material Code	Dry Film Thick- ness mils	Conical Mandrel Test At -65°F	Impact Test	Wet Tape Test
#14	0.55	Passes	Passes	Passes
#14	0.55	"	"	Blister failure
#14	0.6	"	"	N.T. *
#14	0.2	"	"	Passes
#14	0.25	"	"	"
#23	0.1	"	"	N.T. *
#23	0.5	"	"	Passes
#23	0.1	Passes	"	"
#15 20% MEK Thinner	0.2	Passes	Very slight failure	"
#15 No thinner	0.25	"	Passes	"
#15 30% MEK Thinner	0.5	"	"	"

TABLE IX (CONTINUED)

Primer Material Code	Dry Film Thick- ness mils	Conical Mandrel Test at -65°F	Impact Test	Wet Tape Test
#15 No alodine 70% MEK	0.25	Passes	Thinning to sub- strate but no adhesion failure	Passes
#15 70% MEK	0.25	"	Passes	"
#22	1.7	Slight failure	Cracking to from 0 to .25 " radius	"
#22	0.75	Passes	Passes	Passes
#13	1.3	"	Fails	"
#13	0.75	"	Passes	"
#13	1.4	"	Fails	"
#13	0.75	"	Passes	"
#24	0.85	"	"	N.T. *
#24	0.80	"	"	Fails
#12	0.6	Passes	"	Passes
#12	0.75	"	"	"

TABLE IX (COMPLETED)

Primer Material Code	Dry Film Thick- ness mils	Conical Mandrel Test at -65°F	Impact Test	Wet Tape Test
#12 Thinned 20% MEX	0.6	"	Slight thinning to substrate but no adhesion loss	N.T. *
#12 Thinned 10% MEX	0.4	Passes	Slight thinning to substrate but no adhesion loss	Passes
#12	0.45	"	"	"
#26	0.3	Slight cracking up to 0.25 radius	Passes	"
#26	0.15	"	"	"
#26	0.3	Passes	"	"
#26	0.15	"	"	"

\* N.T. = Not tested

TABLE X CORROSION RESISTANCE OF PRIMER DATA

Primer ID Material Code	Substrate Treatment	Number of Corrosion Sites Per Specimen	General Rank All Substrate Treatments 1 = Best	Specific Rank Individual Surface Treatment 1 = Best
Control MIL-P-23377 #26	MIL-A-8625 Type I	0	1	1
	MIL-A-8625 Type II	0		1
	MIL-C-5541	0		1
Material #12	MIL-A-8625 Type I	23	5	11
	MIL-A-8625 Type II	13		9
	MIL-C-5541	4		5
Material #13	MIL-A-8625 Type I	18	3	10
	MIL-A-8625 Type II	6		6
	MIL-C-5541	10		8
Material #14	MIL-A-8625 Type I	3	4	4
	MIL-A-8625 Type II	7		7
	MIL-C-5541	4		5
Material #15	MIL-A-8625 Type I	0	2	1
	MIL-A-8625 Type II	2		3
	MIL-C-5541	1		2

TABLE XI FLEXIBLE PRIMER DATA - 180° PEEL STRENGTH

SPECIMEN I. D.	MATERIAL CODE	AVERAGE PEEL STRENGTH LBS/IN	SYSTEM RANK - 1 = HIGHEST
12A*	#12	27.3	4.0
12B**		27.3	
12C***		32.0	
13A	#13	20.5	5.0
13B		25.0	
13C		21.8	
14A	#14	30.5	3.0
14B		33.5	
14C		33.5	
15A	#15	35.0	2.0
15B		34.0	
15C		36.0	
16A	#26	46.0	1.0
16B		52.0	
Control Specimens 16C		51.5	

\* A denotes substrate alodine treated per MIL-C-5541.

\*\* B denotes substrate anodized per MIL-A-8625 - Type I (chromic acid).

\*\*\* C denotes substrate anodized per MIL-A-8625 - Type II (sulfuric acid).

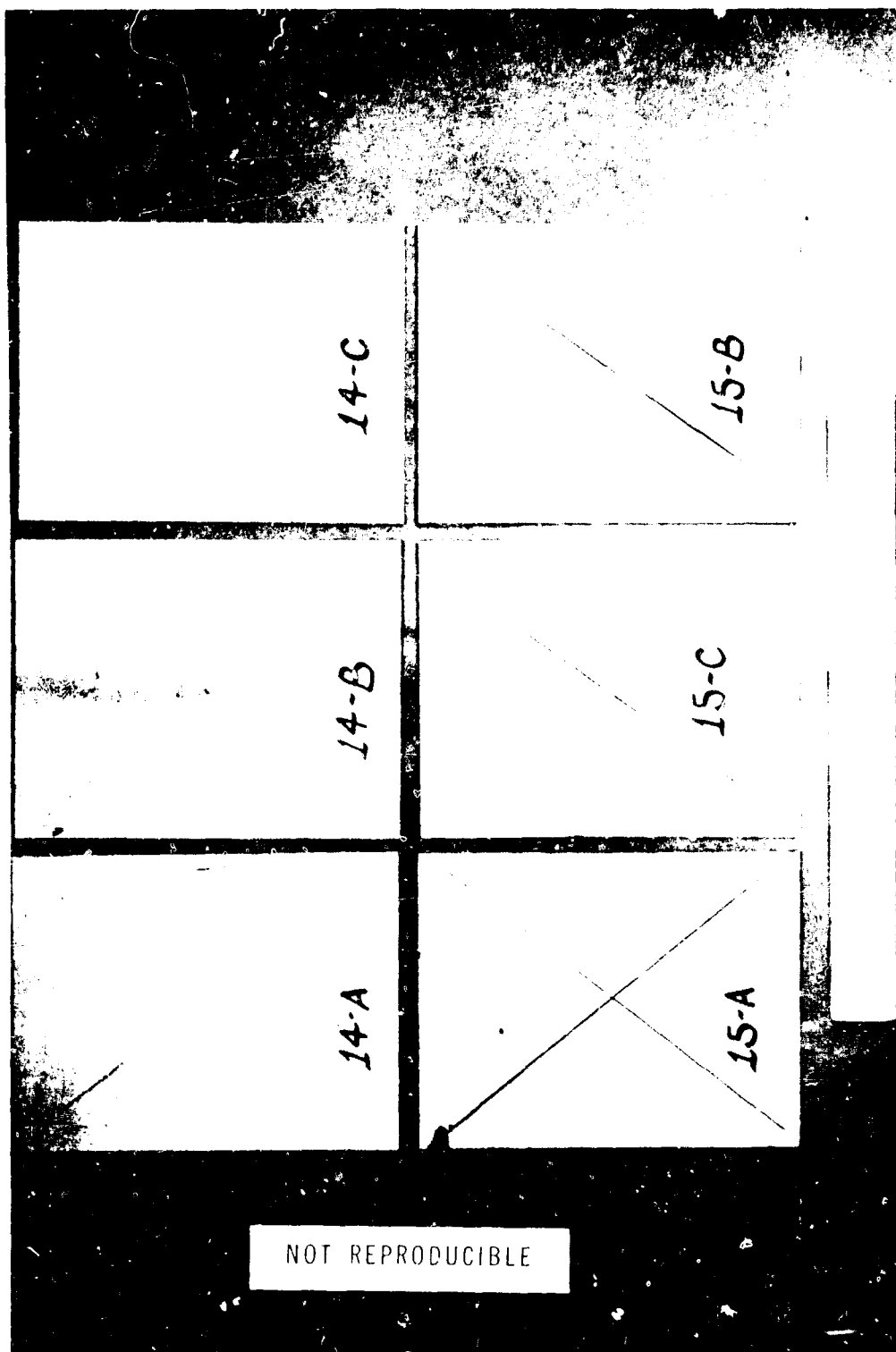


FIGURE 7 SALT SPRAY TEST SPECIMENS AFTER 30 DAYS OF FED TEST STD 141-6061; SUBSTRATE PRETREATMENT:  
A = MIL-C-5541 ALODINE, B = MIL-A-8625 - TYPE I, C = MIL-A-8625 - TYPE II

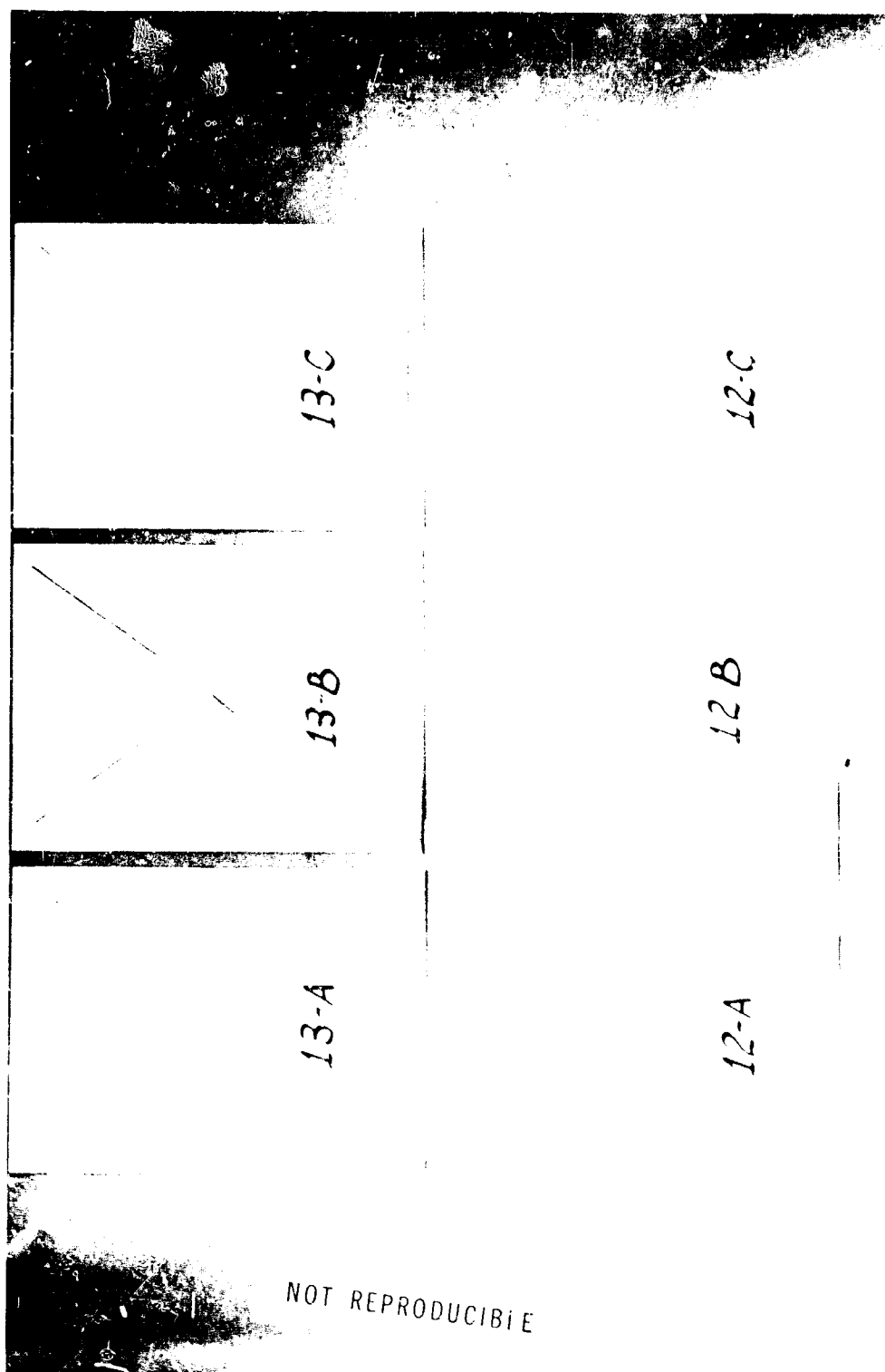


FIGURE 8 SALT SPRAY TEST SPECIMENS AFTER 30 DAYS OF FED TEST STD 141-6061; SUBSTRATE PRETREATMENT:  
A = MIL-C-8541 ALODINE, B = MIL-A-8625 - TYPE I, C = MIL-A-8625 - TYPE II



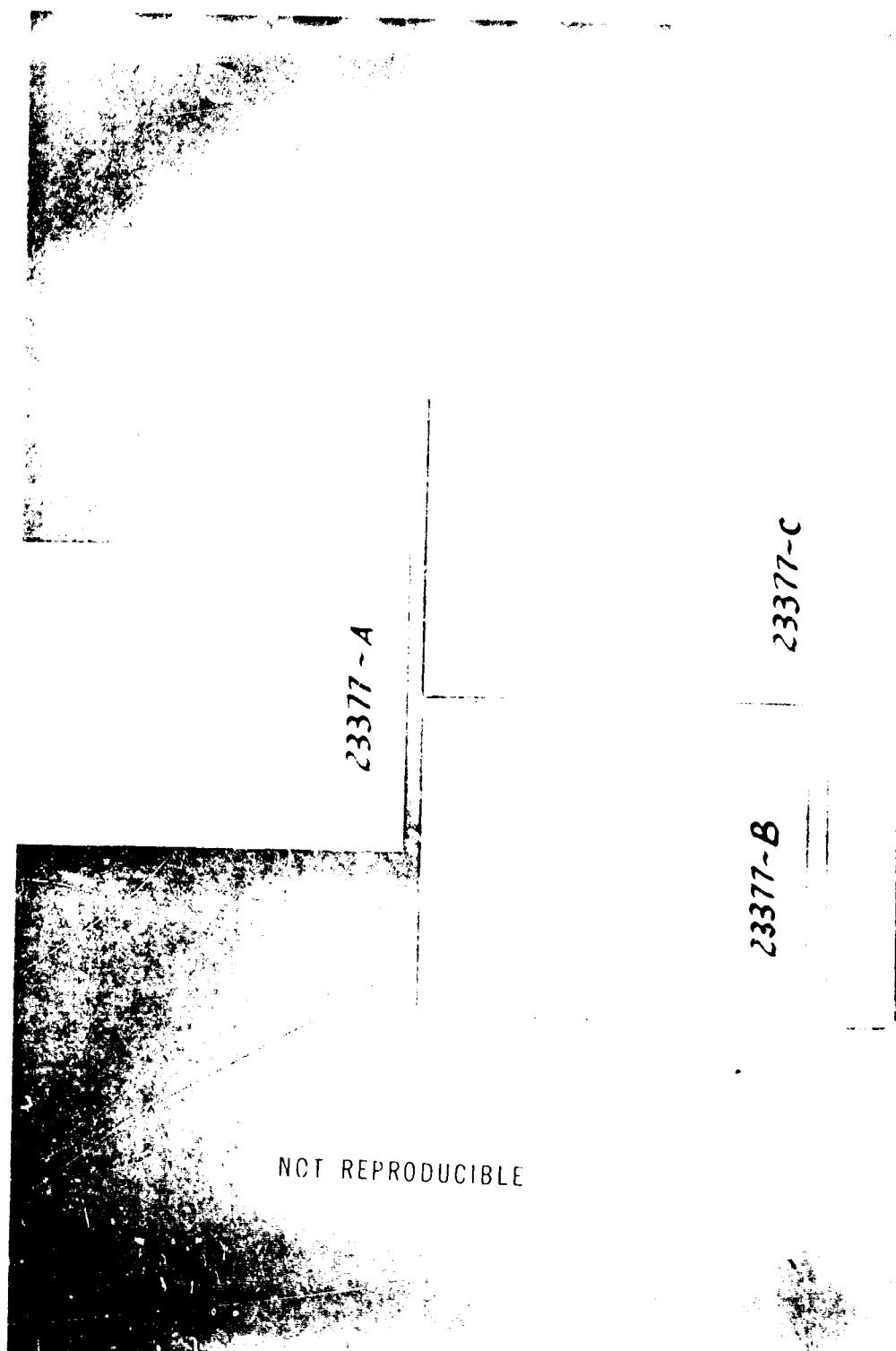


FIGURE 9

CONTROLS MIL-P-23377 EPOXY POLYAMIDE PRIMER, SALT SPRAY TEST SPECIMENS AFTER 30 DAYS OF FED  
STD 141-6061; SUBSTRATE PRETREATMENT: A = MIL-C-8541 ALCLDINE, B = MIL-A-8625 - TYPE I,  
C = MIL-A-8625 - TYPE II

The HS-1 material formulation compounded especially for the hot-vapor carrier (Zicon) spray equipment permitted relatively high rates of coating build per pass. Coating films were deposited that ranged from 4 to 7 mils per pass. These were easily deposited using this formulation and the Zicon equipment. Some edge roughness was observed in test panels and also on production assemblies coated at VAC using the strip coating techniques. Strips sprayed over fastener rows with no masking at the terminal edge of the coating strip had a slight roughness at this point. This roughness was difficult to "hide" with the finish enamel top coat. Materials formulations compounded with reduced viscosity and surface tension alleviated the problem of the rough terminal edge of these coatings. Two additional modified-viscosity compounds (MSA and MSB) were formulated which partially retained the high build character of the HS-1 formulation and produced dry films that were much smoother than those obtained with the HS-1 formulation. More volatile solvents, for faster solvent release was used in the MSA and MSB compounds which permitted overcoating while allowing only five minutes between successive coats of these materials, as compared to the fifteen to thirty minutes required with the HS-1 formulation to allow the less volatile solvents to escape from the coating. An outer wing tip from a salvage F8 aircraft was used for spraying test areas with the low viscosity (MSB) material utilizing conventional suction cup spray equipment, and the quality of the coating obtained in this trial was equally effective in sealing fastener heads as that obtained using the Zicon equipment and the HS-1 formulation. The appearance of this coating was superior to that applied with the Zicon gun using the HS-1 formulation. Figure 10 and Figure 11 depicts fastener countersink patterns coated on the salvaged F8 wing tip. Figure 10 is of the coating applied in two cross coats with five minutes between passes; this area was not overcoated with a finish enamel. Figure 11 is on an area adjacent to that shown in Figure 10. This area was coated at the same time as was the area shown in Figure 10. Figure 11 depicts the MSB elastomer overcoated with approximately 2 mils of MIL-C-81773 polyurethane enamel top coat.

A material formulation identified as HS-1M was formulated which proved to be almost identical to the HS-1 with respect to spraying characteristics such as build per pass, viscosity and spray equipment required. This compound produced dry films that were smoother than those produced with the HS-1 formula. The accumulative build rate was faster for the HS-1M compound than that of the HS-1, since use of a more volatile solvent in the HS-1M permitted application of successive coats with less time required between successive coats than that required in application of the HS-1 compound. Test panels coated with the HS-1M material had a much smoother surface finish than those produced with the HS-1 material.

Pertinent compounding data related to all materials formulations were included in Table II and application information concerning these materials was compiled in Tables II and III of the Appendix.

Capacitance data for salt water permeation studies for various elastomers were compiled in Table VI above.

UNCOATED

NOT REPRODUCIBLE

VEMCO

FIGURE 10 F8 WING-TIP FASTENER COUNTERSINKS 5.0 TO 7.0 MILS MSB ELASTOMERIC POLYURETHANE  
SPRAYED 2 CROSS COATS WITH CONVENTIONAL CUP GUN  
NO-ENAMEL TOP COAT

COATED

NOT REPRODUCIBLE

VEMCO  
PASADENA, CALIF.

FIGURE 11

FL1 WING TIP FASTENER COUNTERSINKS 5.0 TO 7.0 MILS MSB ELASTOMERIC  
POLYURETHANE COATED SAME AS FIGURE 7 AREA  
TOP COAT APPROXIMATELY 2.0 MILS MIL-C-81773 LINEAR POLYURETHANE ENAMEL

### 3.7 RESULTS OF SERVICE OF TECHNOLOGY DEVELOPED (Task VII)

#### 3.7.1 Inspection of Fleet Aircraft Previously Coated

A written report and photographs describing the condition the experimental coating (M9 formulation) applied to three (3) RF-86 aircraft at VAC during the previous contract (N00019-69-C-0132) was received from VAC Field Engineering - unfortunately only one aircraft, #144613, was available for inspection; it was reported earlier by VAC Field Engineering that this ship was assigned to sea duty, and that it was not available for inspection. Contrary to this report however, a written description and photographs of Bureau #144613 aircraft was obtained:

When glancing at the UHT with the unaided eye, there is no noticeable difference as far as corrosion is concerned.

No corrosion was observed on either UHT inspected at VFP-63. Paint on the L/H UHT appears to be thicker than that on the right UHT.

Photographs of the ship were included in Figures 12 and 13 of this report.

#### 3.7.2 Service Application Study

3.7.2.1 Commercial "trial batches" of the M9 low solids material and the HS-1 high solids material were compounded in order to determine the feasibility of producing these materials in greater than small laboratory quantities.

These materials were found to have poor storage stability and some spontaneously polymerized in the can. Tests were performed which directly relates the presence of free water in the compound to this short storage life of these compounds. Laboratory-compounded batches of these materials proved to be quite stable and were useable after seven months storage at room temperature.

3.7.2.2 Commercial batches of the HS-1 high solids material formulation were compounded successfully. This commercially manufactured materials were used to spray test panels satisfactorily. The storage stability of these materials was quite good. Accelerated aging tests at elevated temperatures spoiled these materials after 168 hours at temperatures ranging from 150 to 180°F. These data were included in Table XII.

3.7.2.3 Freezing of precatalyzed premixed polymers of various generic classification has long been an accepted practice in industry; this practice eliminates the need for semi-skilled or technical personnel to mix these materials just prior to use. This allows mixing of a large quantity of material in a centrally located, well equipped mixing room or sealant lab for dispensing in small quantities for use when needed. Quick freezing of the catalyzed material to approximately -45°F retards the rate of the chemical reaction so that materials may be stored frozed for extended periods of time, to be thawed and used without additional mixing. Laboratory and commercial lots of the HS-1 formulation were quick frozen for evaluation in this manner.



FIGURE 12 SHOWS LEFT UNIT HORIZONTAL TAIL UNIT COATED WITH THE '99 ELASTOMER AFTER APPROXIMATELY 9 MONTHS FLEET SERVICE



FIGURE 13 SHOWS CLOSE-UP VIEW OF UHT OF BU. #144613 F8 AIRCRAFT  
COATED WITH THE M9 ELASTOMER AFTER APPROXIMATELY 9 MONTHS  
FLEET SERVICE

NOT REPRODUCIBLE

TABLE XII EFFECTS OF ELEVATED TEMPERATURE TO THE  
SHELF LIFE OF VARIOUS POLYURETHANE ELASTOMERS

Material Type	Test Temperature (Degrees F)	Test Duration (Hours)	Pretreatment Before Test	Results and/or Remarks
Low solids commercial mfg.	180	1.0	2.5% H <sub>2</sub> O added with shaking	Lid blew off after 1 hour due to CO <sub>2</sub> production - Test terminated
M-9 low solids	180	1.0	2.5% H <sub>2</sub> O added with shaking	Lid expanded to hemis- pherical configuration after 1 hour - test termn.
HS-1 high solids	180	1.0	2.5% H <sub>2</sub> O added with shaking	Lid expanded to hemis- pherical configuration after 1 hour - test termn.
RW-608-83 (HS-1) commercial mfg.	180 Room temp.	1 167	"	Material catalyzed form- ing a solid rubber
HS-1	150	168	Purged with dry N <sub>2</sub> prior to seal- ing container	Material completely poly- merized to a solid rubber after 168 hours heating
RW-608-83 HS-1 commercial	"	"	"	"
M-9 low solids	"	"	"	Material contained very small lumps. The viscosity of the base material had increased. The admixed material had a pot life shorter than normal and the admix failed to reach an ultimate cure stage



TABLE XII (COMPLETED)

Material Type	Test Temperature (Degrees F)	Test Duration (Hours)	Pretreatment Before Test	Results and/or Remarks
Low solids commercial mfg.	150	168	Purge with dry N <sub>2</sub> before sealing container	Material contained very small lumps. The viscosity of the base material had increased. The admixed material had a pot life shorter than normal and the admix material failed to reach an ultimate cure stage
"	"	"	"	"
M-9 low solids	"	"	Sealed with ambient atmos- phere inside container	"
Low solids commercial mfg.	"	"	"	"
HS-1	"	"	"	"
HS-1	Room temp.	168	2.5% moisture added with shaking	Polymerized to solid after 168 hours

(1) Laboratory samples were catalyzed, mixed, placed in a plastic container and frozen in liquid nitrogen. After 15 minutes in liquid nitrogen the samples were placed in a -40°F freezer for a period of approximately 72 hours. The frozen cartridges were thawed and the material sprayed. Addition of extra solvent was necessary in order to spray the material, and since the material was of sprayable viscosity before freezing, some polymerization was indicated by the increase in viscosity. A slight grainy or lumpiness was also observed in the finish after application. The material cured faster than usual, again indicating partial polymerization had taken place. The conclusion was made that the frozen material would not remain stable for sufficient time to be useable.

(2) Commercial samples of frozen material (HS-1 high solids) were made at about the same time as was the laboratory material. The commercial material was frozen in a dry ice-solvent slurry and shipped in an insulated package with dry ice inside. Samples of the commercial frozen material were generally comparable to the laboratory material. Additional solvent had to be added in order to restore the original viscosity of the mix for spraying. The lumpiness or grainy texture observed in the laboratory frozen material was also observed in this material.

(3) These tests indicated that quick freezing of the precatalyzed, premixed material does not effectively retard the rate of reaction of this compound to prevent a partial reaction of the material and a subsequent increase of the viscosity of the mix.

3.7.2.4 Free Diisocyanate Content Analysis - A short analytical technique for determining the free diisocyanate content of the basic resin (diisocyanates) used in formulation of this elastomer was included in Table IV of the Appendix. This procedure was included for use to detect low diisocyanate content of the basic prepolymers used in compounding of these elastomeric polyurethanes. This procedure permitted discarding prepolymers that have been contaminated with free moisture (the cause of low diisocyanate) before compounding the resin with pigments. Moisture contamination has caused spontaneous polymerization of materials in the containers, poor storage life and resolution of materials applied.

#### 4.0 CONCLUSIONS

- o Long term aging of the elastomer in natural sunlight reduces the mechanical properties of the elastomer slightly; however, the elastomeric polyurethane withstood the effects of weathering and the associated mechanical damage better than the polysulfide or silicone materials tested.
- o Specimens of the elastomeric polyurethane overcoated with a linear color stable polyurethane top coat withstood the effects of natural weathering in short term tests showing no abnormal adverse effects.
- o The vapor carrier-type spray equipment evaluated for application of relatively thick sag-free coatings is ideal for application of very thick coating films; this equipment is not required to apply the last generation coatings developed as a result of this program.
- o Excellent corrosion protection was afforded the fastener/countersink areas by the unruptured polyurethane coatings.
- o Coating builds of 3-4 mils per cross-coat pass can be applied using the medium solids materials developed with conventional suction cup spray equipment.
- o Color stable (i.e. non-yellowing) elastomers developed during this program cured too slowly for use in room temperature coatings applications.
- o Manufacture of the coating material can be satisfactorily performed in commercial manufacturing facilities, and these materials produce results comparable to those obtained from laboratory-size material lots.
- o Fasteners installed in countersink seats previously coated with the elastomer tend to work loose as design loads are applied. Although a good seal is effected around the fastener and no damage is caused the coating by fastener installation, this technique can not safely be employed in the manufacture of high performance aircraft.
- o Selected fastener patterns can be coated without the use of masking devices by spraying the terminating boundaries surrounding the perimeter of the coating to a feathered or tapered edge.
- o Coatings applied by the feather-edge technique were more aerodynamically smooth and were more easily overcoated by the finish top coat without the attendant hiding problems encountered as in the case when masking was utilized.
- o Costs of applying this sealant system were reduced by approximately 20% as a result of developments allowing deletion of masking surrounding fastener patterns to be coated.
- o No abnormal problems in the service life of this material system have been encountered with any aircraft coated with this sealant to date. This includes F8 aircraft described in this report, as well as A7 aircraft currently being produced at VAC which are protected by this sealant system.

## 5.0 RECOMMENDATIONS

5.1 Development of a flexible elastomeric primer to complement this sealant system should be considered.

5.2 Efforts to synthesize a color stable elastomer should not be relinquished at this time.

5.3 The effects of compounding colors into the elastomeric materials developed to date should be explored.

5.4 A test and evaluation program designed to improve strippers for use in removal of polyurethanes should be considered.

APPENDIX  
MATERIALS REFERENCE NOMENCLATURE

# MATERIALS REFERENCE NOMENCLATURE

1. MOCA, 4, 4 Methylene bis (2 Chloroaniline)
2. DABCO, 1, 4 Diazabicyclo (2, 2, 2) Octane
3. MDA, 4, 4' Methylene dianiline
4. 14491, solution of stannous octoate by Whitco Chemical Co., Fomrez C-2
5. 14492, solution of stannous octoate by Whitco Chemical Co., Fomrez C-4
6. XP-57-28, An aliphatic diisocyanate prepolymer by the Upjohn Co., CPR Division
7. L-2699, An aliphatic diisocyanate prepolymer by E. I. duPont de Nemours Co.
8. CN-15, Polyol by Arco Chemical Co.
9. R45-HT, Polyol by Arco Chemical Co.
10. CS15, Polyol by Arco Chemical Co.
11. R45-7, Polyol by Arco Chemical Co.
12. PR-420, a commercial pigmented polyurethane primer by Products Research and Chemical Corporation
13. PR-1560, same as 12 above.
14. D-513-J-714, a modified epoxy pigmented commercial primer by Desota Inc.
15. H-9924 - chemglaze acid wash primer by Hougson Chemical Co.
16. Polyurethane Elastomer - AML-P7, Manufactured by Hougson Chemical, Erie, Pennsylvania
17. Sprayable Polysulfide Elastomer - EC 1675(S), manufactured by 3M, St. Paul, Minnesota.
18. Silicone Elastomer, DC 92-009, manufactured by Dow Corning, Midland Michigan.
19. Phosphate - Chromate Chemical Treatment - Alodine 100, manufactured by Amchem Products, Ambler, Pennsylvania
20. DETA, diethylenetriamine, manufactured by Matheson, Coleman and Bell, Norwood, Ohio
21. NIAX Polyol D-510, manufactured by Union Carbide Corp., Chemicals and Plastics Division, New York, New York.

22. PR 1060, a commercial pigmented polyurethane primer by Products Research and Chemical Corporation.
23. DC-8-5066, a reactive silane in solvents, by Dow Corning.
24. XAB-975/976-Thixon, a polyurethane, Whittaker Corporation of Dayton Chemical Products Division.
25. XAB-936-Thixon, same as 24.
26. Epoxy Polyamide Primer, MIL-C-22377, by Desoto Inc.
27. Polyurethane enamel, MIL-C-81773, by Finch Paint and Chemical.

TABLE I

## ZICON COATING APPLICATION EQUIPMENT

TYPE GUN	TYPE FEED	FLUID NOZZLE	FLUID NEEDLE	SPREADER	SURFACES COATED
40C-B1	Pressure	R-5	R-5	RB6A2	Vertical Surfaces and Top and Bottom Sides of Horizontal Surfaces
400B-2	Gravity	R-5	R-5	RB6A2	Vertical Surfaces and Top Sides of Horizontal Surfaces



TABLE II

RECOMMENDED COATING VISCOSITY LIMITS FOR USE WITH  
ZICON SPRAY EQUIPMENT (REF TABLE I, APPENDIX)

## COATING VISCOSITY - SECONDS

Max	Nominal	Min.	Method and Temperature 77°F
25	15	10	Per #5 Zahn Cup
--	74	58	Per #4 Ford Cup
500	300	200	Centipoise
5.0	3.0	2.0	Poise

RECOMMENDED COATING VISCOSITY LIMITS FOR USE WITH  
CONVENTIONAL SPRAY EQUIPMENT (REF TABLE III, APPENDIX)

## COATING VISCOSITY - SECONDS

Max	Nominal	Min.	Method and Temperature 77°F
12	10	7	Per #5 Zahn Cup
65	58	45	Per #4 Ford Cup
240	200	140	Centipoise
2.4	2.0	1.4	Poise

TABLE III  
CONVENTIONAL COATING APPLICATION EQUIPMENT

TYPE GUN	TYPE FEED	FLUID TIP	FLUID NEEDLE	AIR CAP
JGA-502	Suction	AV 601 EX	JGA 402 DEX	MBC-4039-30
			MBC 496 DEX	MBC-4039-30
MBC-510	Pressure	AV 601 EX		
			MBC 44 FX	AV 1239-704

TABLE IV

ANALYSIS PROCEDURE FOR ISOCYANATE CONTENT OF PREPOLYMERS

FREE ISOCYANATE

Reagents

Toluene Reagent Grade Only : This material must be free of water.

Dibutylamine approximately 1N. Introduce 120 grams of refined di-n-butylamine into a 1000-ml. volumetric flask. Dilute to the mark with dry toluene, and mix thoroughly.

Procedure

Introduce 25 ml. of dry toluene into a sufficient number of 250-ml. glass-stoppered Erlenmeyer flasks to make all blank and sample determinations in duplicate.

Pipette 20 ml. of the dibutylamine reagent into each of the flasks and swirl to effect complete solution.

Reserve two of the flasks for the blank determination. Calculate the sample size from the following:

$$\text{Wt. sample (grams)} = \frac{42}{\text{estimated NCO, \% by wt.}}$$

Introduce the sample weighed to the nearest 0.1 mg. into each of two flasks and swirl to effect solution.

Allow the samples and blanks to stand at room temperature for 30 minutes.

To each flask add 100 ml. of anhydrous isopropanol, one ml. of 0.1 per cent solution of bromophenol blue indicator in methanol, and titrate with standard 0.5 N-HCL to the first yellow end-point.

Calculation

$$\frac{(B-A)N \times 4.20}{\text{wt. sample}} = \text{free NCO, \% by weight}$$

A = ml. of N normal HCl required for the sample

B = ml. of N normal HCl required for the blank

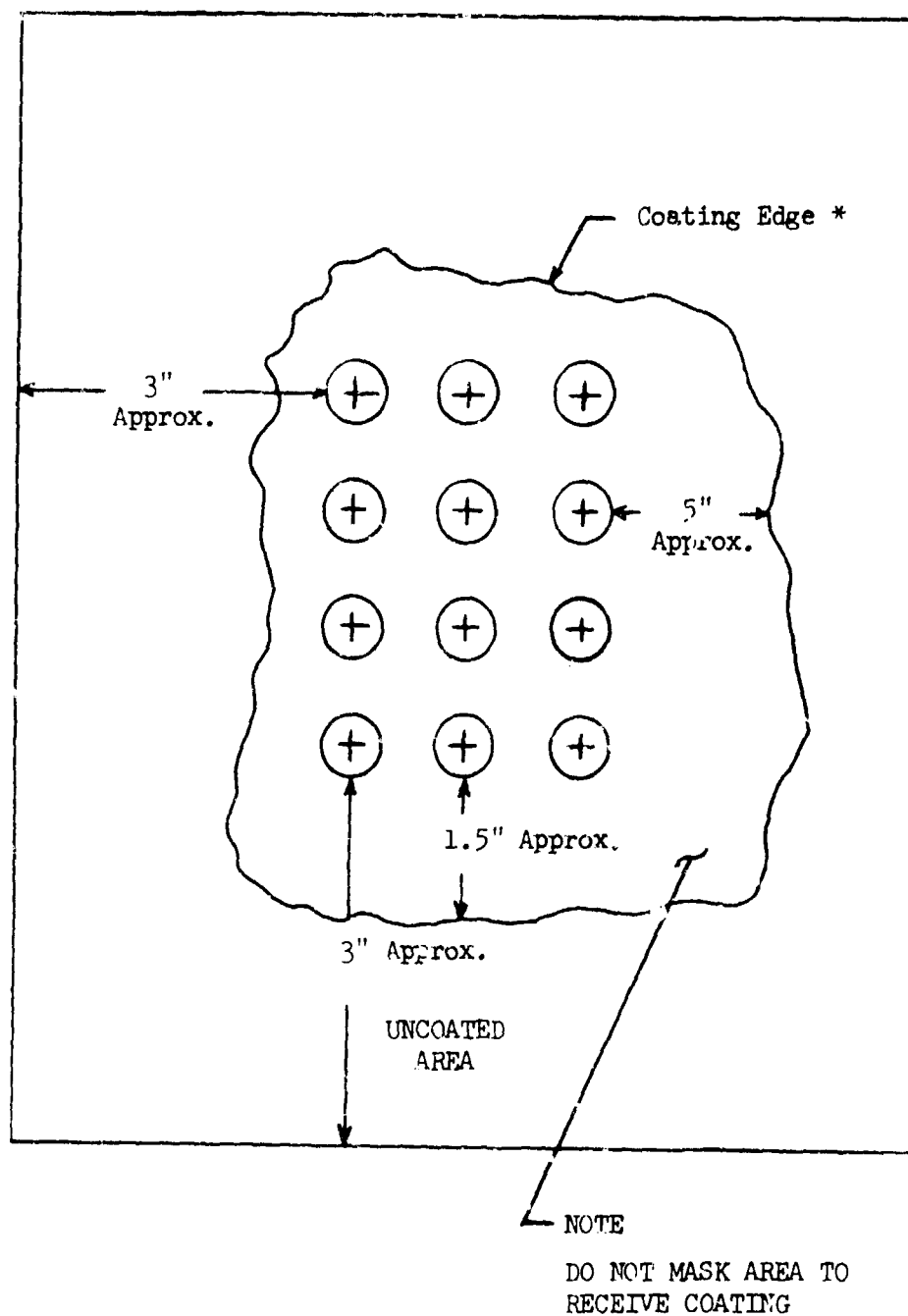


Figure 1  
Typical Coating Application

\* See schematic of a typical feather-edged strip, Figure 2 text

